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Mitre Corp, McLean, Va

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Compilation and Evaluation of Leaching Test Methods

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COMPILATION AND EVALUATION OF LEACHING TEST METHODS

by

William Löwenbach
MITRE Corporation
McLean, Virginia 22101

Contract No. 68-03-2620

Project Officer

Donald E. Sanning
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report is basically a compilation of leaching test methods but it also provides an insight into useful application and interpretation of these tests for further evaluation under the overall USEPA program effort being carried out under a grant to the University of Wisconsin.

ABSTRACT

Under the Resource Recovery and Conservation Act of 1976, EPA is required to promulgate criteria for identification of hazardous wastes. One method of identification is to characterize the leachability of the waste. This study evaluates those factors important to the design of such a test. Additionally, existing leachate tests are compiled and from this listing three tests have been recommended for further evaluation.

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SECTION 1

INTRODUCTION

LEGISLATIVE AND REGULATORY REQUIREMENTS

One of the major objectives of the Resource Conservation and Recovery Act of 1976 (P.L. 94-580) is to regulate the management of hazardous wastes. According to section 1008, the EPA is to develop guidelines which shall "describe levels of performance, including appropriate methods and degrees of control (for solid waste management) that provide at a minimum for (A) protection of public health and welfare; (B) protection of the quality of ground waters and surface waters from leachates; (C) protection of the quality of surface waters from runoff through compliance with effluent limitations under the Federal Water Pollution Control Act, as amended; (D) protection of ambient air quality through compliance with new source performance standards or requirements of air quality implementation plans under the Clean Air Act, as amended; (E) disease and vector control; (F) safety; and (G) esthetics."

Section 3001 explicitly directs the administrator of the EPA to "develop and promulgate criteria for identifying the characteristics of hazardous wastes and further, to list hazardous wastes which will be subject to the provisions of the act." These regulations are to take into account toxicity persistence, degradability in nature, potential for accumulation in tissue and other related factors such as flammability and corrosiveness.

Thus, as part of a protocol to classify a particular waste as hazardous, it is proposed first to examine that waste in terms of characteristics such as reactivity, flammability, corrosiveness, infectiousness, and radioactivity. If the waste is determined to be non-hazardous with respect to the above criteria, the waste is further examined in terms of its leachability in a sanitary landfill under natural conditions. This second stage of testing involves generation of a leachate from the waste in the laboratory (in a manner consistent with those natural processes which occur in a landfill) together with a subsequent evaluation of this leachate. Properties which might be used to define the hazards associated with this leachate include toxicity, carcinogenicity, mutagenicity, and teratogenicity.

OBJECTIVES AND APPROACH

At present, there is no standard method for extracting a leachate from a solid material. Moreover, those processes which govern leachate formation within a landfill are only poorly understood. As an initial step in the development of a standard protocol for leachate generation, the MITRE

Corporation/METREK Division has surveyed existing extraction methods as used by various industries and academic institutions for assessment of leachate. The purpose of this document is (1) to identify those mechanisms which most significantly affect leaching within a natural landfill; (2) to relate these mechanisms to a laboratory leachate test; (3) to compile the results of the above survey, along with other available information; (4) to critically evaluate the various methods; and (5) to provide three candidate interim standard leaching tests which shall be further tested as part of a separate grant to the University of Wisconsin.

Test protocols have been obtained in the following ways:

(1) ASTM committee D19 sent approximately 200 questionaires to its members and other parties who expressed interest in solid waste leachate generation method standardization. The results of that survey (19 responses) have been compiled.

(2) Offices responsible for regulation of solid waste within state environmental agencies have provided test methods which are either in current use or under consideration for adoption as a standard method.

(3) The literature has been surveyed for applicable leachate generation methods.

To critically evaluate laboratory leachate generation methods, it is first necessary to consider leaching under natural conditions. From such a consideration, those parameters which most effect leachate generation and quality may be identified and evaluated from both a theoretical and practical viewpoint. Test methods may then be assessed in terms of the above criteria. Finally three test protocols which promise to best model natural leachate generation will be selected.

BACKGROUND TO SLT DEVELOPMENT

Definition of Relevant Parameters

Leachate is liquid which has contacted solid material and has extracted and/or suspended constituents from it. Whenever water comes into direct contact with solid materials, the potential for leaching exists. Many species exist in solid materials which may be readily soluble in water. Still others may be solubilized by the action of leachate upon them. Thus, character of the leachate depends upon both the composition of the material and on environmental factors.

The principal concern of leachate assessment is not simply which pollutants are released to the environment, but, rather, the rate at which these pollutants are released. Because the kinetic rate expression for leaching is extremely difficult to write from purely theoretical considerations, this data is best obtained experimentally. Once a leaching rate is known, various

modeling techniques may be used to describe the transport of this leachate into the surrounding media.

The materials which are grouped together in the category of solid wastes contain a wide range of organic and inorganic components. While Table 1 lists typical analyses of six industrial wastes, analyses of other wastes may be entirely different. Furthermore Table 1 concentrates specifically on inorganic components, and organic species (identified only as volatile matter in Table 1) are also important factors in determining the potential hazard of a waste.

Environmental factors which exert a strong influence on the character of leachate include pH, the redox potential, the chemical composition, (i.e., hydophobicity, ionic strength, etc.) and temperature. Factors which primarily affect leachate transport, i.e., the rate of leachate generation, include the flow rate of the eluant and the surface area, porosity, and permeability of the material being leached. The definitions and significance of these and other relevant parameters are briefly discussed in Table 2.

General Methods of Leachate Generation

An ideal leaching test then, in order to be meaningful and reproducible, should control those parameters discussed in Table 2 and furthermore should be quick and inexpensive. Additionally, the test should yield information regarding the equilibrium concentration of the important constituents of the leachate, the total amount of each constituent available for leaching from the waste, and the kinetics of the solubilization reactions, including the dynamic changes in leachate composition as various compounds are totally leached from the waste.

No single existing leachate test fulfills all of these requirements. Existing tests fall into three main categories. They are shake (or batch) tests, column tests, and field cell tests. Shake tests consist of placing a sample of the material to be leached in a container with a suitable eluant, agitating the mixture for a specific period of time and analyzing the resulting leachate. This technique can be designed to yield a variety of equilibrium concentrations, depending on the duration of the test, the liquid to solid ratio, and the particle size of the waste. Additionally such a test might conceivably be designed to yield kinetic data if the leachate is sampled at suitable time intervals. An alternate approach to obtaining kinetic data from a shake test is to repeatedly extract the sample with fresh eluant. Shake tests have the advantages of being quick (up to 96 hours), simple (i.e., minimal equipment requirements), and inexpensive. Shake tests are also likely to be the most reproducible of the three types of tests since all variables can be carefully controlled. However, data concerning reaction kinetics are somewhat difficult to obtain from a shake test; furthermore, even though the variables of a shake test may be relatively easily controlled, the conditions chosen may be difficult to relate to environmental conditions in a landfill. As a result, the analyses obtained from such tests may be difficult to interpret.

TABLE 1

INDUSTRIAL WASTE CHEMICAL ANALYSIS[1]

WASTE CELL NUMBER	REFINERY SLUDGE	BATTERY PRODUCTION WASTE	ELECTROPLATING WASTE	INORGANIC PIGMENT WASTE	CHLORINE PRODUCTION BRINE SLUDGE	SOLVENT BASED PAINT SLUDGE
Total Solids[2]	21.00	10.75	20.47	48.25	75.89	75.25
Total Volatile Solids[2]	31.00	7.94	8.98	22.25	1.17	55.31
Moisture[2]	79.00	89.25	79.53	51.75	24.11	24.75
Cr	125	155	1.56[2]	0.50	5.00	75.0
Ni	23	32	35	10	65	0.5
Cu	3500[3]	1125	100	110	125	2.0
Fe	5560	2950	1.37[2]	1000	2000	150
As	1.0	72	460	3.4	14.5	12.8
Be	4.8	1.8	0.25	20.2	<1.0	<1.0
Se	26.0	180	4.50	16.0	16.5	7.60
Cd	0.50	29.0	38.5	10.5	0.70	0.50
Cn	1.0	4.2	460	3.4	14.5	12.8
Pb	182	3.48[2]	267	120	697	12.6
Cl[2]	2.35	1.12	1.35	10.0	20.0	0.75
Asbestos[4]	3.00	208	23.0	45.0	110	9.00
Hg	10.6	4.80	14.7	7.60	227	16.7
Sn		6800				
Sb		1.32[2]				
Clay Volatile Fibers[4]	40.0	720	86.0	185	480	65.0
Zn						
V		120		40		
B	7.20	8.10	19.0	28.5	1.70	11.4
Ti					<0.1	

[1]All values in ppm unless otherwise specified.

[2]Percent by wet weight.

[3]Underlined values indicate maximum sludge concentrations.

[4]Fibers/100 g.

Source: U.S. Environmental Protection Agency, 1976. Residual Management by Land Disposal, Proceedings of the Hazardous Waste Research Symposium, EPA-600/9-76-015. Cincinnati, Ohio.

TABLE 2

DEFINITION AND SIGNIFICANCE OF FACTORS AFFECTING LEACHATE GENERATION

FACTOR	DEFINITION	SIGNIFICANCE	REMARKS
pH	pH is defined as the negative log of the hydrogen ion concentration. pH is an indirect measure of the electro-chemical potential of protons.	The hydrogen ion concentration is an important factor affecting reaction rate and thus pollutant solubilities.	The pH of rainwater is controlled primarily by dissolved CO_2. With rare exceptions, proton exchange and associated processes occur so rapidly that such systems may be treated in terms of shifts of true equilibrium.
pe/E_H	pe is the negative log of the electron activity of a solution. E_H is the redox potential of a system as defined by the Nerst equation. In natural systems E_H is taken as the measured potential difference between an inert electrode (Pt) and a reference electrode.	pe is an intensity factor and measures the oxidizing intensity of a system. The redox potential E_H is a measure of the oxidizing capacity of a system. pe and pH are useful as master variables and provide a framework within which redox and hydrolysis reactions may be compared.	pe and E_H determine, in part, the aerobic or anaerobic conditions under which a material is leached. Large positive values of pe (low electron activity) represent strongly oxidizing conditions while small or negative values (high electron activity) correspond to strongly reducing conditions. pe is a theoretical concept and difficult to measure in the environment. E_H is more easily determined, but may not yield true equilibrium values.
Buffer Capacity	The buffer capacity of a system is defined as the response of that system, in terms of pH change, to the addition of an acid or a base.	Buffer capacity defines the resistance of a system to changes in pH upon the addition of acids or bases.	Naturally occurring leachate exists as a highly buffered system. Total acidity and alkalinity together with pH operationally define buffering capacity.

TABLE 2 (CONTINUED)

FACTOR	DEFINITION	SIGNIFICANCE	REMARKS
Complexation Capacity	Complexation is defined as the formation of a complex from a metal ion with a natural or negative ion by means of one or more chemical bonds.	The effects of complexation vary from increasing the solubility of specific metals to causing their precipitation, depending on the complexing agent and the metal ion. Complexation affects the solubilities, reactions and modes of transport of leached materials.	The most effective complexing agents are generally organic compounds. Fulvic and humic acid are two naturally occurring complexing agents of possible significance in terms of heavy metal transport.
Ionic Strength	The ionic strength of a solution, I, is defined as $I = \frac{1}{2}\Sigma C_i Z_i^2$, where C_i is the concentration of an ion in moles per liter, Z_i is its charge and the sum is taken over all ions in the solution.	Ionic strength has a significant effect on reaction rate and therefore influences the solubility of ionic species. In general the solubility of an ionic salt is roughly proportional to $\sqrt{I}$ for dilute solvents.	The ionic strength is generally calculated rather than measured directly. The ionic strength together with the dielectric constant define in part the polarity of a medium.
Dielectric Constant	The dielectric constant is defined by ϵ in the equation $F = \frac{QQ'}{\epsilon r^2}$ where F is the force of attraction between two charges Q and Q' separated by the distance r in a uniform medium.	The dielectric constant is related to the solvating power of the eluant. It increases with addition of ionic species. Polar substances become more soluble with increasing dielectric constant, while non-polar substances become less soluble.	The dielectric constant of a system is determined by both the molecular nature of the system (e.g., polarizability) and the composition of the system. The dielectric constant together with ionic strength define in part the polarity of a system.
Temperature	Temperature is an intensive property of a system and defines the direction of heat flow between systems. A systems temperature, in part, defines the energy available to the system.	Temperature affects both the solubility and more importantly the rate of reactions. Thus, changes in the temperature of a system may change the reaction mechanism.	Temperature within a landfill varies significantly with seasonal temperature changes; furthermore natural systems are not likely to be in complete equilibrium due to local energy fluxes within the landfill.

TABLE 2 (CONCLUDED)

FACTOR	DEFINITION	SIGNIFICANCE	REMARKS
Surface Area	The surface area is somewhat difficult to define operationally but practically involves the measurement of some property that qualitatively depends on the extent of surface development and can be related (by means of theory) to absolute surface area. Suitable methods of determination include particle or pore size measurement and permeability studies.	Heterogeneous reactions of solids and liquids are often governed by a surface process that occurs at a rate directly proportional to the surface area of a solid, in addition to the reagent concentration in the liquid phase. Finely divided particles have a greater solubility than large crystals. The surface energy of particles smaller than -1μ may become large enough to effect surface properties.	Different methods of surface area measurement will lead to different result. For the purpose of discussing leachate generation within a landfill, methods based on permeability studies or particle size measurement are most useful. Particle size of materials deposited in landfill usually decreases with time due to physical and chemical weathering processes.
Liquid to Solid Ratio	The liquid to solid ratio may be defined for both a landfill and a laboratory leachate test. The ratio is best defined by the weight ratio of an eluant to the solid.	Increasing the liquid to solid ratio will increase the total amount of species leached; conversely, a low liquid to solid ratio will minimize the amount of species leached but will lead to higher concentrations of the most soluble species.	The liquid to solid ratio is difficult to define for natural systems; moreover any such ratio defined will vary significantly with time. In a laboratory test this ratio will determine the importance of common ion effects.
Contact Time	The amount of time (residence time) between an eluant and the solid leached.	Maximum species concentrations (in a batch test) will occur upon the attainment of equilibrium. Equilibrium is a unique thermodynamic state of a system depending only on temperature; as such, this state provides a framework within which comparisons to other systems may be made.	True equilibrium, or even steady state conditions, are unlikely to be reached in natural systems. For such systems the extent of reaction (related to equilibrium) may be a more useful concept than equilibrium per se.

Column tests are performed by placing the material to be leached in a column, with or without a quantity of fill material from a landfill. Eluant is allowed to flow through the column, the rate of flow being proportional to the head (height of water in the column) and the permeability of the material. Advantages of column tests include low cost, minimal equipment requirements and a generally more accurate simulation of kinetic factors affecting environmental systems than is obtained by shake tests. The major disadvantage is the length of time required to yield meaningful results, generally in the range of months to years.

Field test cells are controlled scale models of actual waste disposal sites, usually employing extensive monitoring systems. Field tests are the most accurate method of determining the quality and quantity of leachage entering the environment under the specific test conditions. However, they are expensive, time consuming, and highly site-specific.

Due to the requirements for a quick and inexpensive test, current research emphasis is focused on the shake test. Therefore, the remainder of this document is primarily devoted to a discussion of those factors which most affect the design of a shake test.

SECTION 2

THEORETICAL CONSIDERATIONS OF LEACHATE GENERATION

INTRODUCTION

Leachate generation, whether under natural or well-controlled conditions (i.e., in the laboratory), is exceedingly complex. The description of interactions between an eluant and a solid phase, even at the most rudimentary level, necessitates an understanding of heterogeneous equilibria; furthermore, both the eluant and solid phase are complex heterogeneous systems in their own right. Additionally because such systems, in general, will contain both organic and inorganic matter, chemical characterization is difficult at best.

Currently, available chemical data and phenomenological models are unable to accurately predict the distribution of species in leachate much less the kinetics of leachate generation; furthermore, it is doubtful whether any attempt to describe such systems in full detail will ever be complete. However, useful insights may be gained by application of equilibrium, and where possible kinetic, models to simple homogeneous and heterogeneous systems. Where kinetic information is not available, (and it is generally not) equilibria models at least provide boundary conditions within which discrepancies between observed conditions and the models may be resolved. Thus the major value of the phenomenological model presented below will lie in the comparative format in which the following questions may be asked: (1) What is the basic mechanism of leachate generation? (2) What are the most important factors, i.e., the controlling chemical reactions, in leachate generation? (3) And finally, how should a laboratory test be designed so as to yield the most useful information for prediction of leachate generation in the field?

THERMODYNAMIC RELATIONSHIPS

One common definition of equilbrium (with respect to a particular reaction in a closed system) is, "that state attained when a reaction is allowed to proceed in the 'forward' direction (left to right) until there is no net change in the composition of the system and then to allow the same reaction to proceed in the 'backward' direction until again no net change is observed"; if chemical equilibrium is reached, the composition of the system will approach the same limit from both directions. However many systems, notably organic and redox reactions, do not reach equilibrium over short time spans. For these systems only kinetic and mechanistic descriptions will suffice. Nevertheless, for a large number of reactions there is sufficient evidence (kinetic and equilibrium) to justify consideration of real systems at the equilibrium state.

Equilibrium Model for Leachate Systems

With the preceding discussion serving as a brief review of those elements of thermodynamics necessary for development of equilibrium models, it is now possible, in theory at least, to consider the real and complex systems which occur in the natural environment. However, before discussing the more realistic models, it is useful to discuss chemical equilibria within the conceptually simpler framework of a closed system. In general such a system (see Figure 1) consists of a gas phase, an aqueous phase, and a specified number of solid phases of defined compositions. To develop a rigorous thermodynamic definition of such a system, information about concentrations* (or more accurately activities), and pressure is required.

Construction of an isothermal, isobaric thermodynamic model is, in theory at least, relatively straight forward. The system is first defined in terms of relevant species and phases. Care must be taken to ensure the thermodynamic self consistency of the system, (e.g., an equilibrium constant for each reaction, the stoichiometry of each reaction specified, a net charge of zero in the solution phase). With the system thus defined and assuming the availability of required thermodynamic data (free energies, equilibrium constants), ΔG is set equal to zero and the composition of the system calculated. To date the only application of this approach has been to inorganic ocean (Kramer, 1965) and fresh water models (Stumm, 1970; and Morel and Morgan, 1972).

The above requirements are deceptively simple. It is not a trivial task to identify pertinent reactions and equilibria of all types require careful examination because of their influence on pH, buffering capacity (both pH and pε), and adsorption of inorganic and organic species. Complex formation equilibria between all possible ligands and cations of interest must be considered. Where the redox equilibria of multivalent elements (e.g., the transition metals, nitrogen) are considered, the situation becomes even more confused; competing redox systems can often lead to pseudo-equilibrium conditions.

More important, are the inherent limitations of any thermodynamic treatment. Reactions predicted to be thermodynamically favored (i.e., a large negative ΔG) need not occur at observable rates. Familiar examples include most organic reactions; the decomposition of acetic acid,

$$CH_3COOH \rightleftharpoons 2H_2O + 2C$$

is predicted to be highly spontaneous ($\Delta G = -17.9$) but because of the lack of a suitable kinetic pathway does not proceed at an observable rate. The lack of any required relationship between the thermodynamics and reaction rates simply means that while thermodynamic models may provide boundary values for such systems, kinetic considerations may render such answers of little practical significance.

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*For a rigorous derivation of the relationship between activity and concentration, see Moore (1972), page 307.

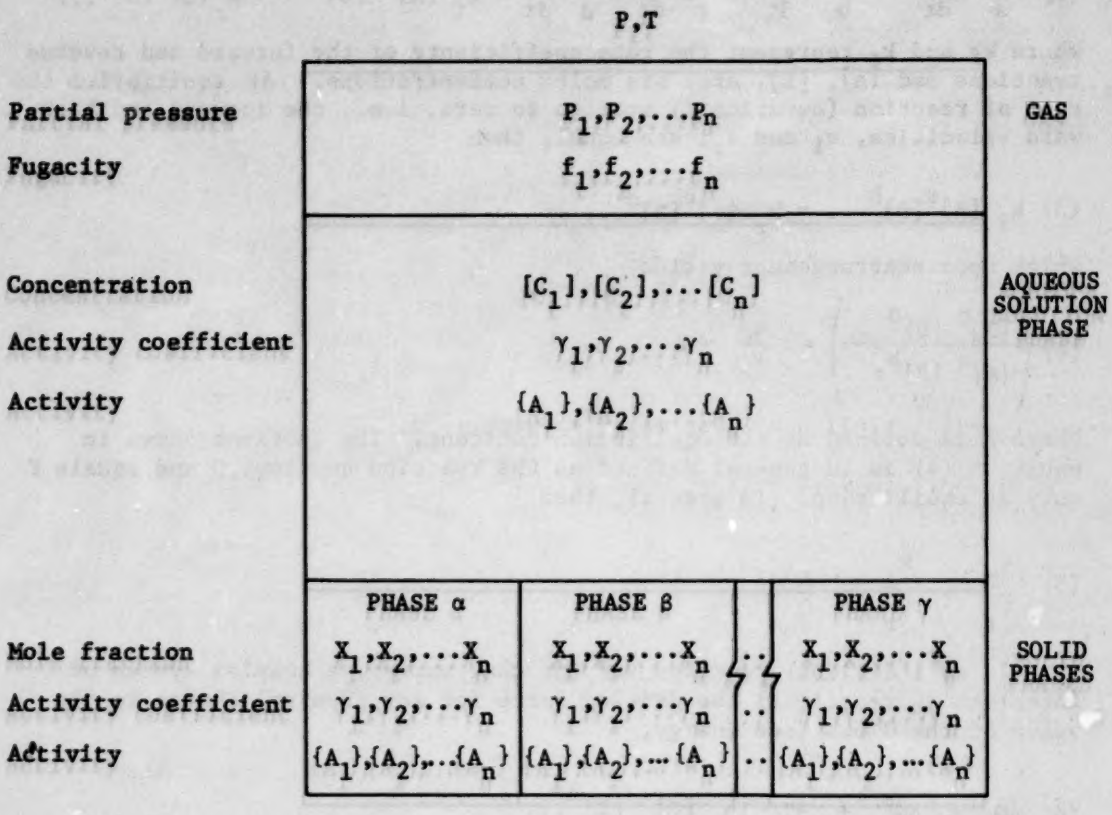


FIGURE 1. GENERALIZED MODEL FOR THERMODYNAMIC DESCRIPTION OF LEACHATE SYSTEMS.

Consider the chemical reaction

(1) $aA + bB + \ldots = cC + dD + \ldots$

where a,b,c,d, are the mole numbers of species A, B, C, D, repectively. Furthermore, assume that the rate of reaction may be expressed in the form

(2) $-\frac{1}{a}\frac{dA}{dt} = -\frac{1}{b}\frac{dB}{dt} = \frac{1}{c}\frac{dc}{dt} = \frac{1}{d}\frac{dD}{dt} = k_f [A]^a [B]^b \cdots - k_r [C]^c [D]^d \ldots$

where k_f and k_r represent the rate coefficients of the forward and reverse reactions and [A], [B], etc. are molar concentrations. At equilibrium the rate of reaction (equation 2) must go to zero, i.e., the forward and backward velocities, v_f and v_r, are equal, then

(3) $k_f [A]^a [B]^b \ldots = k_r [C]^c [D]^d \ldots$

which upon rearrangement yields

(4) $\left(\frac{[C]^c [D]^d \ldots}{[A]^a [B]^b \ldots}\right) = \frac{k_f}{k_r} = K$

where K is defined as the equilibrium constant. The quotient shown in equation (4) is in general defined as the reaction quotient Q and equals K only at equilibrium. In general, then

(5) $\frac{v_f}{v_r} = \frac{k_f}{k_r} = \frac{K}{Q}$

In an individual reaction (or for that matter, a complex system of interlocking reactions) the driving force for any chemical change is the value of the Gibbs free energy,

(6) $\Delta G = \Delta G^o + RT \ln \frac{[C]^c [D]^d \ldots}{[A]^a [B]^b \ldots}$

where R is the ideal gas constant and T the temperature in degree Kelvin. At equilibrium, $\Delta G = 0$ by definition and Q is equal to K so that the Gibbs free energy in the standard state is

(7) $\Delta G^o = -RT \ln K$

More generally, under any conditions, from equations (6) and (7) together with the definition of Q,

(8) $\Delta G = RT \ln \frac{Q}{K}$

Dynamic Model for Leachate Systems

Any relevant leachate generation model must, however, be designed as an open system. Figure 2 illustrates the major features necessary for the formulation of a dynamic model for such a system. While in theory any arbitrary model might be studied, the simplest model of a dynamic system is one at a stationary, nonequilibrium state. In contrast to a closed system at equilibrium where $\Delta G = 0$, the stationary state is determined by the fluxes of reactants and products between the system and its surroundings and by the reaction kinetics.

The fundamental expression which describes the concentration, C_i of a constituent i at any point (x,y,z) in a dynamic system is:

$$(9)\quad \frac{\delta C_i}{\delta t} + u\frac{\delta C_i}{\delta x} + v\frac{\delta C_i}{\delta z} + w\frac{\delta C_i}{\delta z} = \frac{\delta}{\delta x} D_x \frac{\delta C_i}{\delta x} + \frac{\delta}{\delta y} D_y \frac{\delta C_i}{\delta y} + \frac{\delta}{\delta z} D_z \frac{\delta C_i}{\delta z} + r_{i,n}$$

where $u\delta C_i/\delta x$ etc. are advective or convective terms, $\delta/\delta x(D_x \delta C_i/\delta x)$ etc. are diffusion transport terms, and $r_{i,n}$ denotes the rate of formation or disappearance of component i by a process n. When component i is at the steady state, then $\delta C_i/\delta t = 0$. Steady state models have been developed for various chemical reactions and in different natural water systems. These models require, however, detailed information on the flows in the system, the rates of chemical reactions in the system, the diffusion and mixing of components, etc. While such models can, in theory, accurately describe the spatial distribution of chemical species involving a combination of slow reactions, high rates of material and energy flow, and complex transport processes within a landfill, the necessary conditions to achieve a stationary state will rarely be realized because of large perturbations in the fluxes of matter and energy.

With the preceeding discussion serving as an overview of the total system, consider now those individual parts of the system which make up the whole as shown in equation (9): transport of species once in solution (all terms containing C_i and the kinetics of species formation ($r_{i,n}$). There are numerous studies concerning the transport of pollutants to the aquatic environment (e.g., Fuller, 1976). While such information is vital for the proper design of a landfill facility, these studies have little bearing on leachate formation per se. For a general review of transport theory, the reader is referred to Gray (1973).

To understand and at least conceptually model leachate generation in complex systems, those kinetic processes and mechanisms which influence leachate composition must be considered; however, because a rigorous kinetic treatment of leachate generation is beyond the scope of this document (and probably impossible for any realistic case), only those factors which significantly affect such modeling will be considered. The following sections, then, are specifically intended to (1) set forth those general principals of

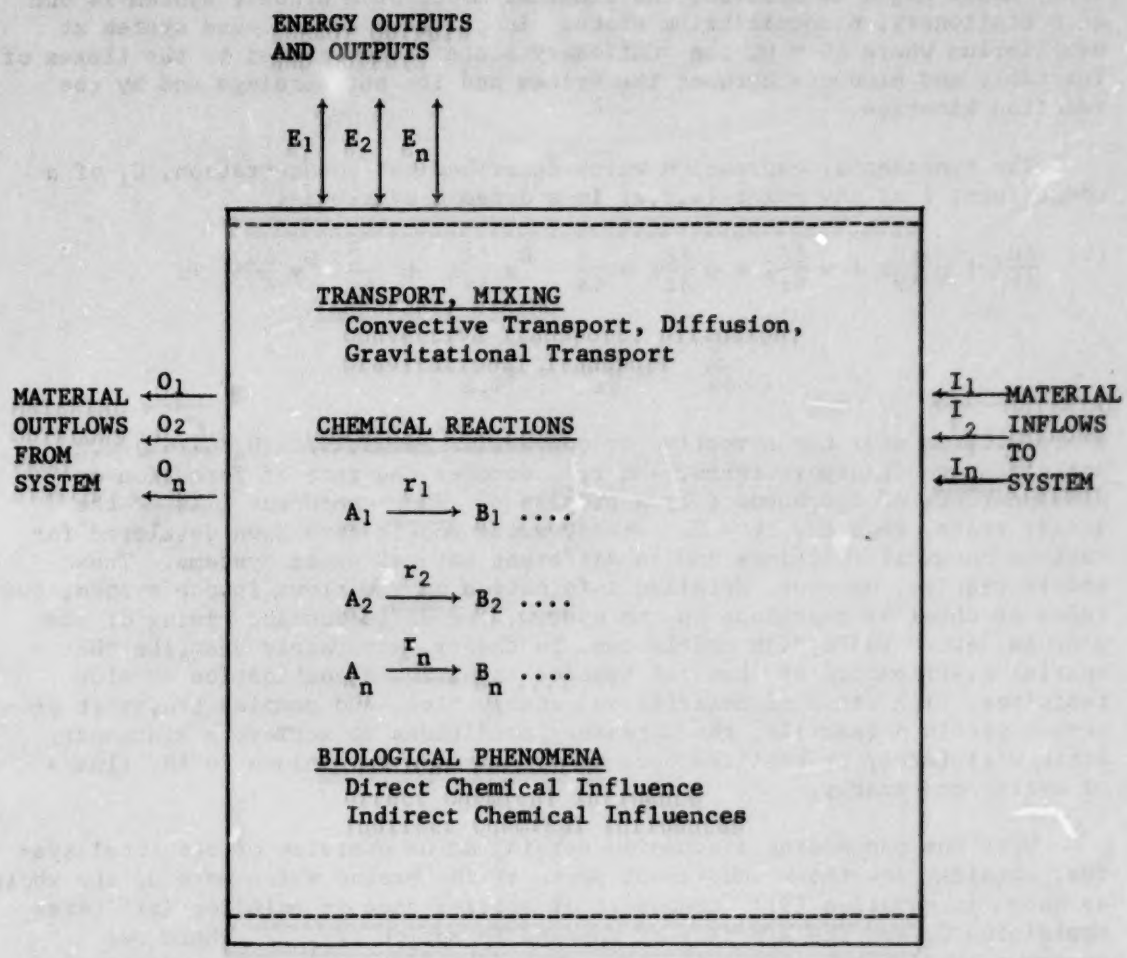


FIGURE 2. GENERALIZED MODEL FOR CHEMICAL DYNAMIC DESCRIPTION OF LEACHATE SYSTEMS.

reactions between solids and water (i.e., physical effects) and (2) discuss, in general terms, those reactions (and those factors which mediate them) affecting leachate composition. More complete understanding of these problems will necessarily come from both laboratory experiments and field observations.

GENERAL KINETIC CONSIDERATIONS

Of necessity, any consideration of the dissolution of a solid phase requires an understanding of heterogeneous equilibria; quite clearly, the nature of the liquid-solid interface will play an important role and the intent here is only to provide a brief discussion of those features which especially involve surface chemistry.

The dissolving of a metal in acid solution (an example of a redox reaction), of silicon dioxide by aqueous hydrofluoric acid (an example of complexation), and of a soluble salt in water (complexation also) are primarily surface reactions that occur at a rate directly proportional to the surface area of the solid. Since, in general, chemical attack is also involved, the reaction rate is also dependent on the concentration of the reagent. It is important to note that either the chemical reaction at the surface may be rate controlling, as is the case with the dissolving silica, or the diffusion of products away from the surface may be the slow step, as is the case with the dissolving of a soluble salt. Because diffusion processes have been extensively discussed by numerous other authors*, and, moreover, because the deliberate direct disposal of large quantities of highly soluble material is presumed to be precluded from proper landfill operation, only the case where the chemical reaction is rate controlling (e.g., as in the case of the dissolution of sparingly soluble salts), will be considered here.

Kinetics of Dissolution Reactions

Most inorganic systems exhibit surface charge along fracture and cleavage surfaces due to the rupture of bonds. When such systems are brought into contact with water, these ions absorb water molecules, which can then dissociate. Dissolution occurs until the equilibrium is established. The extent of a dissolution (or precipitation) reaction most often has been considered for systems at equilibrium because kinetic factors are extremely difficult to assess. Investigations of sparingly soluble salts appear to be limited to the kinetics of crystal growth rather than dissolution. However, if the principle of microscopic reversibility is to apply, the general features of such a mechanism should apply equally to the dissolution of a sparingly soluble salt. Empirically the rate of crystal growth for many salts may be described by an equation of the form (Nancollas and Purdie, 1964)

$$-\frac{dm}{dt} = ks\,(m - m_o)^n$$

where m is the concentration of a species in solution at time t, k is the rate constant, s is the available surface area, and n is a constant. This empirical

*See for example Crank (1956).

relationship, which is also obeyed for certain dissolution reactions, may be interpreted in terms of a mechanism involving a rate controlling surface reaction. A possible mechanism for the dissolution of a solid is shown in Figure 3 in which the overall dissolution process consists of: (1) an initial diffusion of the ion, ion pair, or molecule from a kink site (position A) in the crystal lattice along the step edge to position B which is less stable than position A since only two surfaces are in contact with the crystal lattice. Thereafter (2) the ion or molecule may diffuse to a still less stable site (position C) to the bulk of the solution (position D). Experimental evidence from crystal growth studies point to surface reactions such as (1) or (2) as the rate determining steps rather than bulk diffusion (3) although this need not be the case for dissolution.

Physical Effects

Before discussing the more complex relationship between eluant composition and dissolution rate, it is useful to first consider the kinetic effects of temperature, ionic strength, dielectric constant*, and surface area. While the latter may be for the most part, of somewhat less importance than the eluant composition, such parameters may, under special circumstances outweigh the effects of eluant composition. A simple example would be a landfill which continually remains at temperatures below those necessary to allow appreciable biodegradation.

Temperature

The variation of the equilibrium constant, K with temperature obeys the law

$$\frac{d\ln K}{dT} = \frac{\Delta E}{RT^2} \qquad (10)$$

where R is the ideal gas constant, T the temperature in degrees Kelvin, and ΔE the change in energy. Recalling the relationship between the equilibrium constant K and the rate constants k

$$k_f/k_r = K \qquad (4)$$

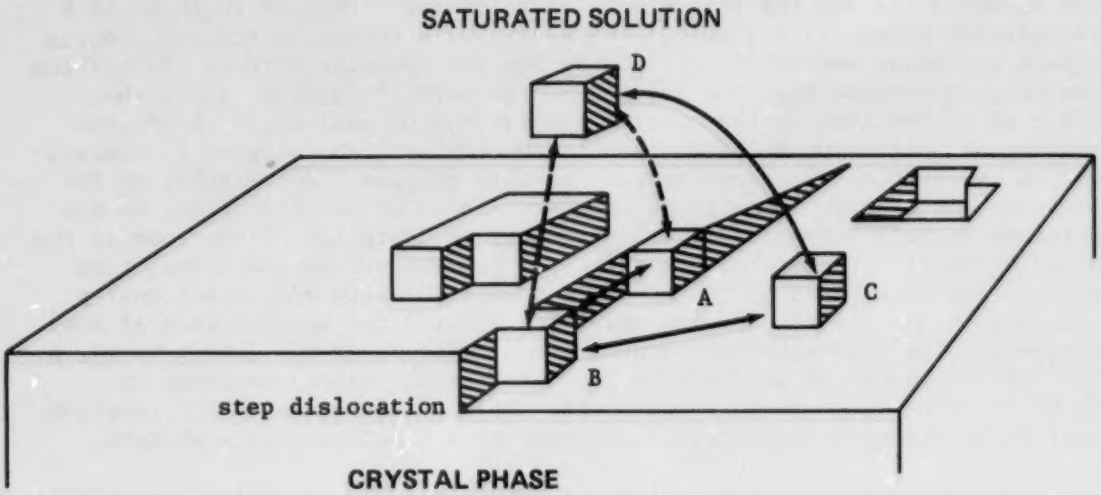
and combining with equation (10) yields

$$\frac{d\ln k}{dT} = \frac{\Delta E}{RT^2} \qquad (11)$$

If equation (11) is integrated and the antilog taken, then

$$k = A\exp(-E_A/RT) \qquad (12)$$

* Although the ionic strength and the dielectric constant are both related to the composition of a given solution, these parameters, for the purposes of this document, are considered to be better described in terms of physical rather than chemical effects.



Source: Nancollus and Purdie, 1964.

FIGURE 3. STEPS INVOLVED IN CRYSTAL DISSOLUTION.

where A is a complex term often described as a frequency factor and E_A is the activation energy; thus as temperature increases so does the reaction rate.* While such treatment is successful in predicting the affect of temperature on many reactions, there are numerous exceptions. As an example, consider the effect of temperature on the two most prevalent reactions in a landfill: simple dissolution reactions (i.e., constant pH and pε) and biological reactions.

The net energy change for a simple dissolution process may, from a thermodynamic viewpoint, be regarded as the sum of the free energy of lattice dissociation and the free energy of solvation. Thus, a large lattice dissociation energy (i.e., $\Delta G > 0$) tends to make a substance insoluble while a large solvation energy**(i.e., $\Delta G < 0$) has the opposite effect. By writing a kinetic expression for each process in the form of equation (12), the effect of temperature on the overall process may be evaluated. Since the breaking of lattice bonds is a dissociation process, an increase in temperature is expected to increase the rate of this process. Conversely, an increase in temperature normally decreases the rate of ion solvation, as the increased kinetic energy of molecules hinders orientation of the ions in the solvation shell. Therefore, the effect of temperature on the dissolution rate will be determined by two opposing terms, the rate of lattice energy dissociation and the rate of ion solvation. While the solubilities of many inorganic salts increase with temperature (dominance of the former term), a number of compounds of interest in leachate ($CaCO_3$, $CaSO_4$) decrease in solubility with increase in temperature. Figure 4 illustrates the relative equilibrium constants of various compounds as a function of temperature.

Temperature has a strong effect on both biological activity and organic reaction rates. For biological systems each microorganism will have an optimum growth temperature, ranging from 0°C to as high as 80°C. Over a short temperature range the growth rate increases with increasing temperature as shown in equation (12). Much above the optimum temperature, however, the growth rate drops to zero since vital enzymes are presumably destroyed. The above argument also applies to organic reactions in general and a common rule of thumb is that a 10°C rise in temperature doubles the reaction rate.

Ionic Strength

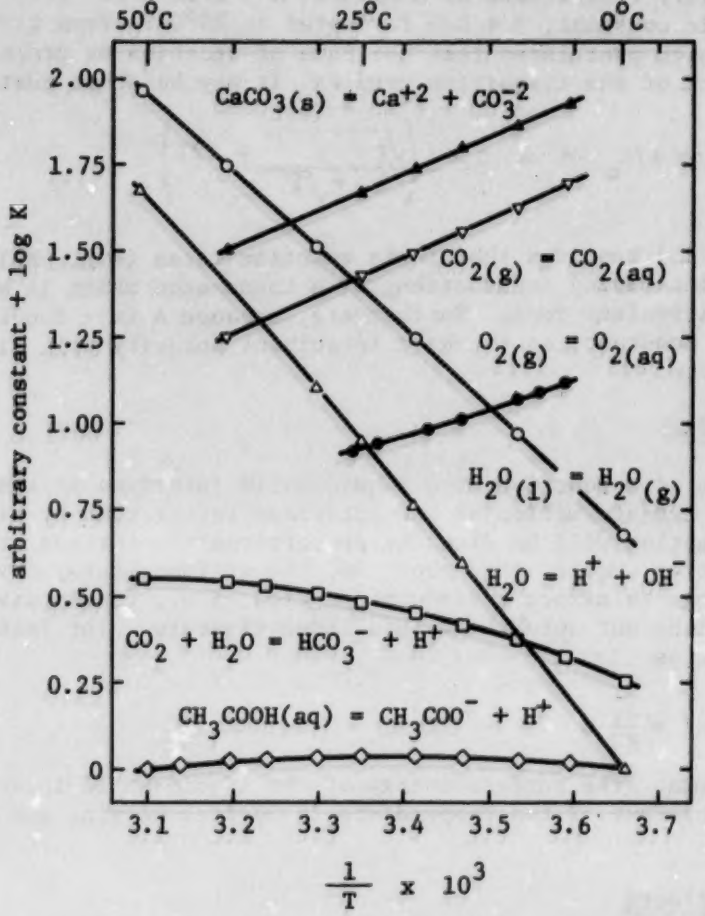
Ionic strength, I, is defined as

$$I = 1/2 \sum C_i Z_i^2 \qquad (13)$$

where C is the concentration and the Z is the ion charge. The latter may be related to the activity coefficient of a solute by a number of empirical expressions. The most useful relationship for relatively concentrated solutions

*This analysis assumes that: (1) the reaction proceeds by a single pathway; and (2) E_A is independent of temperature.

**Solvation energy is defined to include dipole-dipole and dispersion energies as well as a positive entropy term.



Source: After Stumm and Morgan, 1970.

FIGURE 4. RELATIVE EQUILIBRIUM CONSTANTS AS A FUNCTION OF TEMPERATURE.

(~0.5M), is that of Davies:

$$\log \gamma_{\pm} = A\ z_+ z_- \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - .2I \right) \tag{14}$$

where γ is activity coefficient of a solute; $A = 1.82 \times 10^6\ (\varepsilon T)^{2/3}$ (where ε is the dielectric constant; $A \approx 0.5$ for water at 25°C). From transition state theory, which postulates that the rate of reaction is proportional to the concentration of the transition complex, it may be shown that

$$\log k/k_o = A\ z_+ z_- \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - .2I \right) \tag{15}$$

Thus equation (15) requires that ionic reaction rates (e.g., solubility) increase with increasing ionic strength, a phenomenon which is most pronounced for multivalent ions. Furthermore, because A is a function of the dielectric constant, an increase in solvent polarity will also increase the reaction rate.

Particle Size

If the rate of a reaction at a liquid-solid interface is limited by an actual chemical transformation at the interface rather than by diffusion, then rate of reaction will be directly proportional to surface area. However, for particles smaller than about 1μ, the surface energy may become sufficiently large to affect surface properties, i.e., finely divided solids have a greater inherent solubility than large crystals. The latter effect may be expressed as

$$\ln K \approx \frac{2\bar{\gamma}}{RT} S \tag{16}$$

where $\bar{\gamma}$ is the mean free surface energy of the liquid-solid interface, R is the ideal gas constant, T the temperature in degrees Kelvin, and S the molar surface area.

Chemical Effects

Turn now to the more complex task of describing those factors which will control the composition of leachate in the natural environment. In general, for an electrolyte that dissolves in water according to the reaction

$$A_m B_n{}_{(S)} \rightleftharpoons m A^{+n}_{(aq)} + n B^{-m}_{(aq)}$$

the equilibrium condition is

$$A_m B_n{}_{(S)} = m A^{+n}_{(aq)} + n B^{-m}_{(aq)}$$

and the solubility is generallly expressed as the solubility product

$$K = \left[A^{+n}_{(aq)}\right]^m \left[B^{-m}_{(aq)}\right]^n \tag{17}$$

where the activity of the pure solid phase is set equal to unity. Rarely however can the solubility of a salt be calculated from its solubility product alone. The simplest realistic case is illustrated by considering the solubility of a salt in solutions that contain a common ion. Figure 5 is a graphical representation of the solubility product where the log of the metal ion concentration is plotted as a function of the log of the common ion. The solubility may be characterized in this manner because the cations and anions of the illustrated salts do not undergo protolysis reactions to a significant extent near pH 7. Furthermore, complex formation between cation and anion may be assumed to be negligible as long as the free metal ion and the free cation concentration are small. Dashed lines in the figure indicate where the foregoing assumptions are no longer valid.

However, even this case, in which solubility can be calculated from both known concentrations and from the solubility product, is rarely encountered. Dissolved ions frequently undergo chemical reactions in solutions and therefore equilibria other than the solubility product (e.g., complex formation of the cation or anion with one of the constituents of the solution) must also be considered. Additionally, cations and anions may further react with water. As an example, consider the solubility of iron (II) sulfide in aqueous solution containing sulfide anion. Not only the solubility equilibrium, but also the hydrolysis equilibria of the cation,

$$Fe^{+2} + H_2O \rightleftharpoons FeOH^+ + H^+$$

and the anion,

$$S^{-2} + H_2O \rightleftharpoons HS^- + OH^-$$

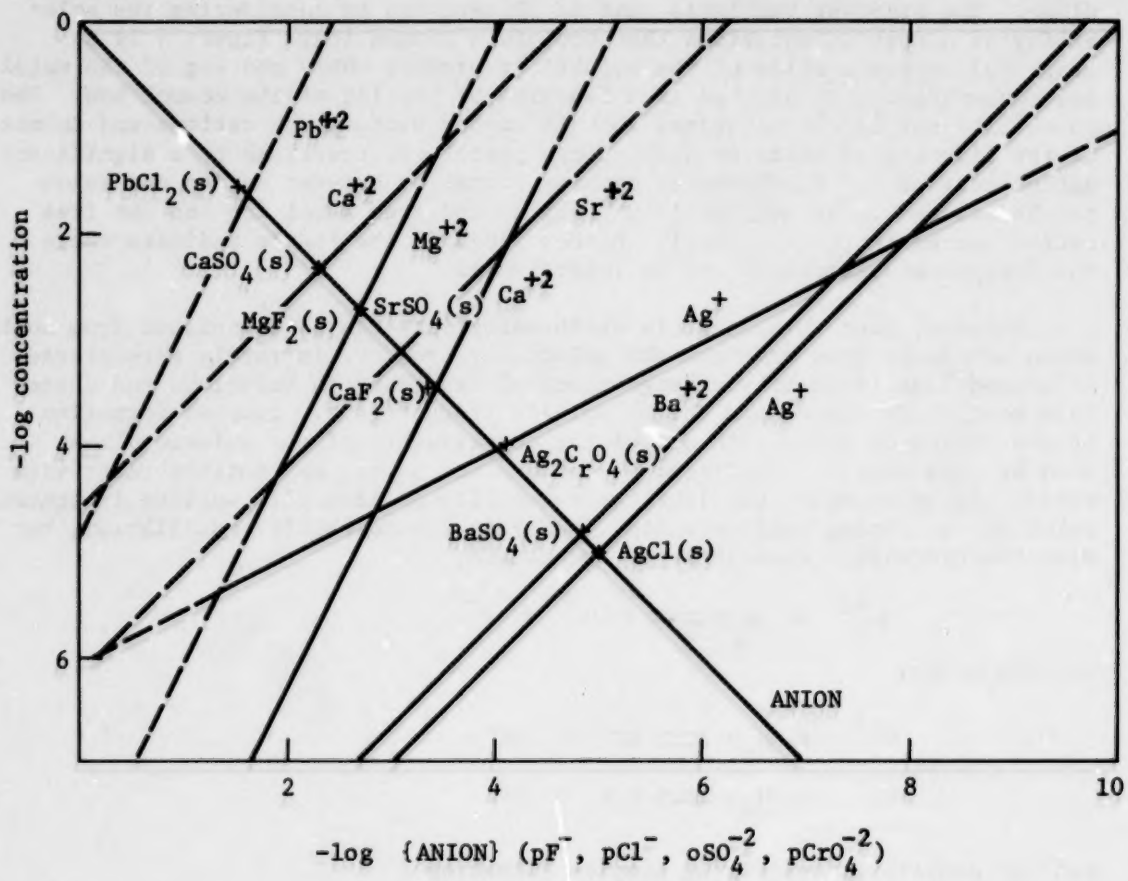
$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$

and the equilibria describing complex formation

$$FeS + S^{-2} \rightleftharpoons FeS_2^{-2}$$

must be taken into account.

Since any realistic discussion of dissolution equilibria soon becomes so complex as to become meaningless, practicality dictates consideration of only those parameters which most affect the solubilities of organic and inorganic solids. These include: the pH of the solution (leachate); the type and concentration of complexing ligands and chelating agents; the oxidation states of the inorganic compounds, and the redox environment of the system. For complex organic constituents (i.e., high molecular weight compounds) biological degradation may well be the most important mechanism of aqueous



Source: After Stumm and Morgan, 1970.

FIGURE 5. SOLUBILITY OF SIMPLE SALTS AS A FUNCTION OF THE COMMON ION CONCENTRATION.

transport. Secondary effects such as adsoption of metal ions from solution by the solid phase and ion exchange are not considered explicitly. The following is a brief discussion of (1) those chemical factors which are relevant to leachate generation in the environment (and hence must be addressed by a laboratory leachate test) and (2) the general mechanisms by which the above factors are likely to control important reactions.

pH

The negative logarithm of the hydrogen ion concentration, or pH, along with the redox environment of the system, is the most important variable controlling leachate composition. Because dissolution occurs in the aqueous phase, pH may be considered as a master variable of the system; that is, any reaction which involves either H^+ or OH^- will be affected by the pH of the medium.* In general, pH may affect dissolution in two principal ways: alteration of simple solution equilibrium and direct participation in redox reactions. An example of dissolution by the first mechanism is the following:

$$CdCO_3 \rightleftharpoons Cd^{+2} + CO_3^{-2} \quad pK_{sp} = 13.74$$

however, in the presence of acid the following action takes place:

$$CO_3^{-2} + 2H^+ \longrightarrow [H_2CO_3] \longrightarrow H_2O + CO_2$$

Thus, a sparingly soluble salt in a neutral solution, may be completely dissolved in a sufficiently acidic one. For a more realistic case, where at least inorganic ligands other than water are present, the speciation of cadmium is a function of pH as shown in Figure 6. Clearly, the formation of insoluble ligand complexes may greatly affect the distribution of metals between the solid and aqueous phases by the formation of precipitates.

The hydrogen ion concentration will also, in part, define the redox potential of the system. For example, the following reaction is rapid in moderately acidic solutions ($\leq$pH 5) but not in neutral solution:

$$Al^o + 3H^+ \longrightarrow Al^{+3} + 3/2H_2$$

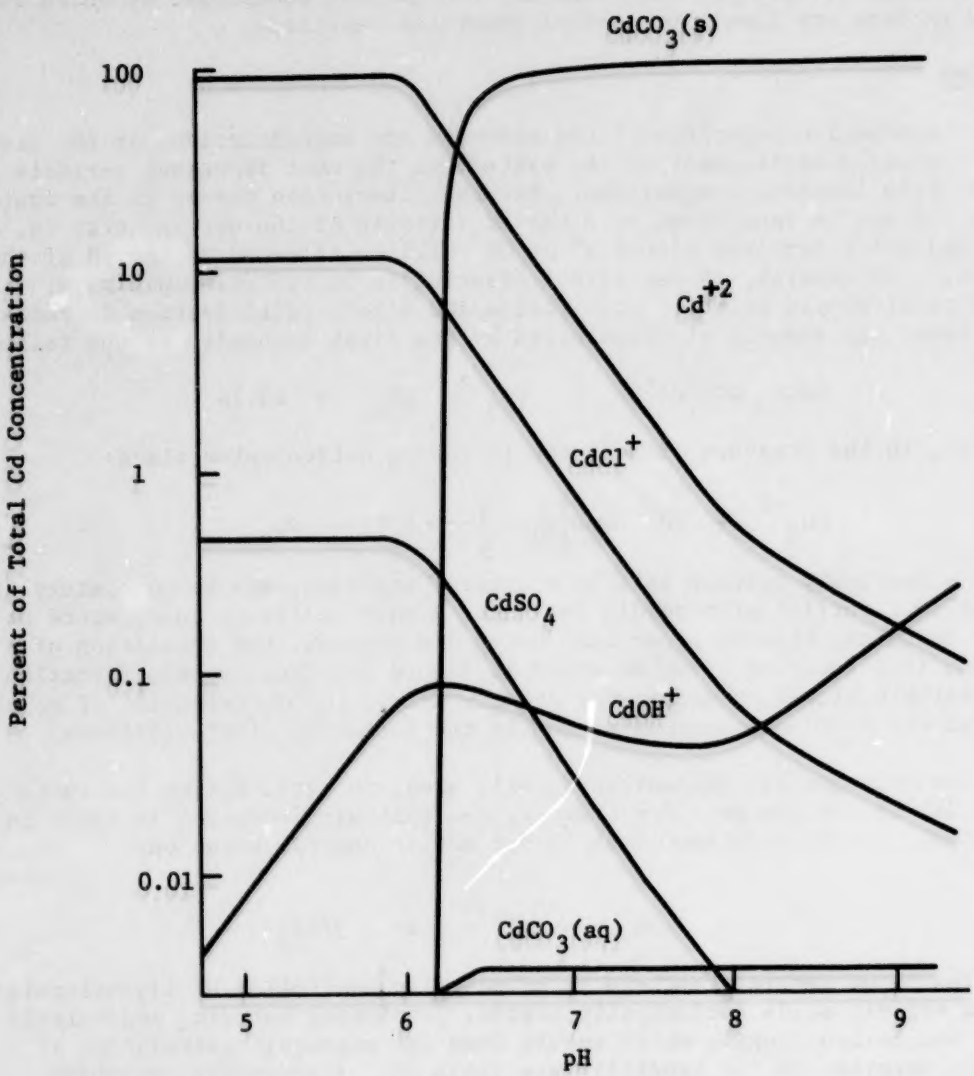
The pH of natural leachate is principally controlled by low molecular weight organic acids (principally acetic, propionic, butyric, and valeric acid) and carbon dioxide which result from the anaerobic degradation of organic material in the landfill (see Table 3). A secondary mechanism which is probably less important in controlling leachate pH is hydrolysis of

*Hydrogen ion [H^+] and hydroxide ion [OH^-] concentration in aqueous solution are related by the equation

$$H_2O \rightleftharpoons H^+ + OH^-$$

where the equilibrium is defined as

$$K_w = [H^+]\,[OH^-] = 10^{-14}$$



Source: Morel et al., 1974.

FIGURE 6. SPECIFICATION OF CADMIUM IN A FOUR LIGAND SYSTEM AS A FUNCTION OF pH.

TABLE 3

ANALYSIS OF THE ETHER EXTRACTABLE[1] ACID PORTION OF YEAR OLD LEACHATE

Constituent[2]	Concentration (g/l)	Percentage of Fraction
Propionic acid	4.5	6
i-butyric acid	16.5	22
n-butyric acid	48.8	65
Valeric acid	5.2	7

[1]Leachate (from which neutral constituents had been removed) was acidified to pH 2 and extracted continuously for 48 hours with diethyl ether.

[2]Analyzed as methyl esters.

Source: Burrows and Rose (1975).

heavy metals. Most highly charged heavy metal ions, e.g., Fe^{+3}, Cr^{+3}, are strongly hydrolyzed in aqueous solution as a result of the dissociation of a coordinated water molecule within the hydration shell of the metal ion. For example, in aqueous solutions, iron (III) hydrolyzes in the following manner:

$$Fe(H_2O)_6^{3+} + H_2O \overset{K_1}{\rightleftharpoons} Fe(H_2O)_5OH^{+2} + H_3O^+$$

and

$$Fe(H_2O)_5\,OH^{+2} + H_2O \overset{K_2}{\rightleftharpoons} Fe(H_2O)_4(OH)_2^{+} + H_3O^+$$

The extent of this reaction is roughly a function of the ionic charge: thus highly charged species such as Hf^{4+} and Th^{4+} are extensively hydrolyzed while ions such as Ca^{+2} and Mg^{+2} hydrolyze only in basic solution.

Hydrolytic products as shown above may also form polymeric species, e.g.,

$$2Fe\,OH^{+2} \rightleftharpoons Fe_2(OH)_2^{4+}$$

Such complexes may vary from small discrete ions to large high molecular weight polymeric compounds; the latter are of considerable interest as they may be regarded as the kinetic intermediates of insoluble metal oxides.

Buffer Intensity

Leachate must be considered as a highly buffered soltuion because the organic acids and carbon dioxide produced by biodegradation will be partially neutralized by basic materials in the landfill. A buffer solution may be operationally defined as a fairly concentrated solution of a weak acid and its conjugate base. While it may be unlikely that any single buffering system is dominant in leachate, to consider further the mechanism of pH control, it is useful to introduce the concept of buffer intensity, i.e., the capacity of the solution pH to remain unchanged despite the addition of either acid of base.

If the assumption is made that the hydrogen ion concentration is small compared to the concentration of the acid [HA] and its conjugate base $[A^-]$, then the pH of the solution may be expressed as

(18)

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

Mathmatically, the buffering capacity, β, is conveniently defined as

(19)

$$\beta = \frac{d\,[A]}{dpH}$$

where A is a strong acid. Thus, the larger the value of β, the better the buffering system. For a monoprotic acid* the buffer intensity is

(20)

$$\beta = 2.303 \left(\frac{K_w}{[H^+]} + [H^+] + \frac{CK_a\,[H^+]}{(K_a + [H^+])^2} \right)$$

where

$$K_w = [H^+]\,[OH^-] = 10^{-14}$$

*An analogous expression may be defined for a polyprotic system.

The dissociation constant of water,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

the dissociation constant of a weak acid HA and,

$$C = HA + A^- \ .$$

For any landfill where acidic and basic solids are present, heterogeneous equilibria must be considered. The buffer intensity for such a system may be defined in an analogous manner where the appropriate solubility equilibria are taken into account. However, whether the system is controlled by homogeneous or heterogeneous equilibria does not affect the utility of the concept of buffer intensity - a measure of the response of the system (in terms of pH) to wastes which are either strongly acidic or basic.

Organic Constituents

A large variety of organic compounds are likely to be present in a landfill. These include natural degradation products of plant and animal matter, (e.g., amino and humic acids) as well as organic wastes. An important characteristic of organic compounds which function as ligands, is their ability to form water soluble and water insoluble complexes with metal ions. Of special concern is the formation of water soluble metal-organic* complexes with toxic metals which may increase the concentrations of these constituents in leachate to levels far in excess of their normal solubilities.

For the complex-formation reactions between metal ions (M) and organic ligands (L)

$$M + L \rightleftharpoons ML$$

the equilibrium constants are

(21) $$K = \frac{[ML]}{[M][L]}$$

---

*The term "metal-organic" is used to define structural configurations in which the metal is bonded to organic matter by (1) carbon atoms (yielding organo-metallic compounds) (2) carboxylic groups (producing salts of organic acids), (3) electron-donating atoms, O, N, S, P, etc. (forming coordination complexes) or (4) π electron ligands (olefinic bonds, aromatic rings, etc.)

(where a monodentate ligand is considered and where charges of the species have been omitted for simplicity). In general, a metal ion will coordinate with more than one ligand and form complexes in a stepwise manner, e.g., Cu^{2+}, $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, $Cu(NH_3)_4^{2+}$, for which an equilibrium constant is defined for each step as above. Furthermore, the concentration of species complexed in solution will be pH dependent since the ligands are generally acids or bases in their own right and thus dissociate according to the equilbrium

$$H_nL \rightleftharpoons H^+ + H_{n-1}L^- \rightleftharpoons \ldots\ldots H^+ + L^{-n}$$

Natural leachate systems, even though well buffered (and thus considered to be at constant pH), are considerably more complex since there are numerous ligands of differing complexing ability competing for coordination of a large variety of metal ions. While computations of the distribution of ionic species in a solution containing many metals and ligands can be done with computers using available programs (Perrin, 1967; Childs, 1969; and Morel, 1970), the following general points will suffice to illustrate the general principles of complexation of metal ions in natural leachates:

(1) Complexes with monodentate ligands are usually less stable than those with multidentate ligands. Also important is that the degree of complexation decreases more strongly with dilution for monodentate ligands than for multidentate ligands.

(2) Metal ions can be buffered (in a manner analagous to pH buffering) by adding appropriate ligands to a metal ion solution*

$$[M] = \frac{[ML]}{[L]}$$

Such buffers resist a change in $[M]$ and are useful for investigating phenomena pertaining to metal ions. If a solution is simply diluted, the activity of the free metal ion may, because of adsorption, hydrolysis, or other side reactions, be entirely different from that calculated by dilution alone.

(3) Where the ligand concentration is small only a "one ligand" complex is likely to be formed.

(4) And ligands, such as humic acids, phosphates, or polyphosphates, when present in concentrations too small to form soluble complexes, may still aid in the formation of stable negatively charged colloidial dispersions.

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*The buffering intensity of M can likewise be defined in a manner analogous to that of the buffering intensity of H^+

Unfortunately, little is known concerning complexation in natural leachate; relatively few studies have even attempted more than a gross identification of organic constituents. Johansen and Carlson (1976), for example, identified and quantified the organic compounds shown in Table 4 in a variety of leachates. Because leachate composition is strongly influenced by site specific conditions (e.g., fill construction, precipitation, age of the fill) the concentrations shown in Table 4 serve only to illustrate the general concentration ranges of organic constituents. Khare and Dondero (1977), in a recent study analyzed leachate for a wide variety of inorganic and organic compounds as shown in Table 5.

Although not identified explicitly in the previous analyses (other than as carbohydrate or protein - Table 4), Chian and DeWalle (1974, 1976, 1977) indicate the possible importance of humic* and fulvic acid**, complexation of metal ions in leachate. While the chemistry of these species is not yet well understood, a variety of structures and reaction mechanisms have been considered. Schnitzer (1976) proposes the chemical structure shown in Figure 7, and notes that this structure is in accord with most empirical results. Stevenson (1976) further suggests the following general features of the reaction mechanism for metal complexation by humic acids:

(1) Carboxyl groups play a prominent role in complexation of metal ions. Mixed complexes are probably formed, the most important of which is of the phthalic acid type. Other possible combinations in order of importance are: a COOH group and a phenolic OH group; a COOH group and a quinone group; and a COOH group and a NH_2 group.

(2) Metals serve to link individual molecules together to produce polymeric structures as shown in Figure 8.

(3) Metal complexes of humic acid are soluble at low metal ion-humic acid (HA) ratios, but precipitation occurs as the polymeric structure grows and the isolated COOH groups are neutralized by salt bridges. Where precipitation occurs, it is a function of factors such as ionic strength, pH, humic acid concentration, and the specific metal ion. Figure 8 illustrates the metal ion: (1) as 2:1 complex linking two groups; (2) as a 1:1 complex and (3) in a salt linkage with an isolated COOH group.

*Humic and Fulvic acids are terms applied to dark-colored, acidic, predominantly aromatic, hydrophilic, chemically complex polyelectrolytes that range in molecular weight from a few hundred to several thousand whose chemical properties are comparable to synthetic polyelectrolytes, such as polyacrylic and polymethacrylic acid; they are best classified on the basis of solubility. If a material containing humic substances is extracted with a strong base and the resulting solution acidified, the products are (1) a nonextractable residue called humin, (2) a material which precipitates from the acidified extract called humic acid, and (3) an organic material which remains in the acidified solution called fulvic acid.

**Humic acids have also been suggested to be important for electron transport in anoxic environments (Schindler et al., 1976).

TABLE 4

DRY WEATHER ORGANIC ANALYSIS OF LEACHATES FROM NORWAY AND THE PACIFIC NORTHWEST[1]

Parameter \ Landfill	NORWAY												U.S.A.			
	Gronmo		Branaasdalen		Yaggeseth		Taranrod		Isi I		Isi II		Cedar Hills		Kent Highland	
	mg/l	mg C/l	mg/l	mg C/l	mg/l	mg C/l	mg/l	mg C/l	mg/l	mg C/l	mg/l	mg C/l	mg/l	mg C/l	mg/l	mg C/l
TOC	100		250		1700		800		180		30					
Total carbohydrate	24	10	37	15	54	22	113	46	57	23	6	2				
Total protein			181	94	144	75			88	46						
Acetic acids	<10		129	52	420	168	421	169	100	40	30	12	2750	1100	300	120
Propionic acids	<10		37	18	231	111	282	136	67	32	<10		4375	2100	380	182
Butyric acids	<10		12	7	681	368	318	172	14	8	<10		5875	3173	260	140
Iso butyric acids	<10		<10		78	42	32	17	<10		<10					
Valeric acids	<10		<10		219	129	87	51	<10		<10		550	324	190	112
Iso valeric acids	<10		<10		241	142	19	41	<10		<10					
Caproic acids													600	372	90	56
Total organics identified		10		185		1057		658		149		14		7069		610

Source: Johnson and Carlson (1976).

TABLE 5

NONVOLATILE AND VOLATILE
CONSTITUENTS OF LEACHATE

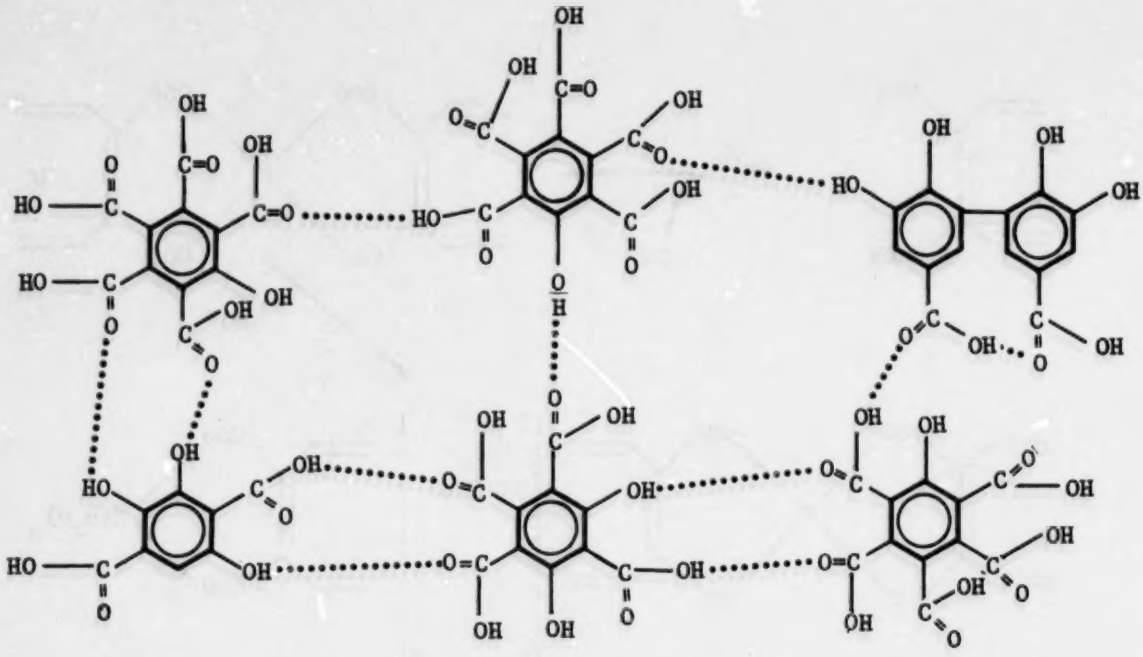
Constituent	Concentration mg/L
Nonvolatile:	
Sodium	136.0
Magnesium	66.0
Aluminum	0.13
Potassium	66.0
Calcium	272.0
Manganese	10.85
Iron	0.81
Copper	< 0.01
Zinc	0.09
Cadmium	< 0.01
Lead	0.03
Total carbon	767.0
Organic carbon	695.0
Inorganic carbon	72.0
Total nitrogen (Kjeldahl)	52.0
Ammonia-N	50.0
Nitrite-N	0.040
Nitrate-N	0.061
Total soluble phosphate-P	0.152
Phosphate-P	0.010
Sulfate-S	39.0
Chloride	205.0
Volatile:	
Methane	Detected but not measured
Ethane	
Ethylene	
1-Pentene	
Hexane	
Heptane	
Nonane	
Decane	
Dodecane	
4-Methyl-1-hexene	
Acetone	
2-Butanone	
Chloroform	

TABLE 5

NONVOLATILE AND VOLATILE
CONSTITUENTS OF LEACHATE

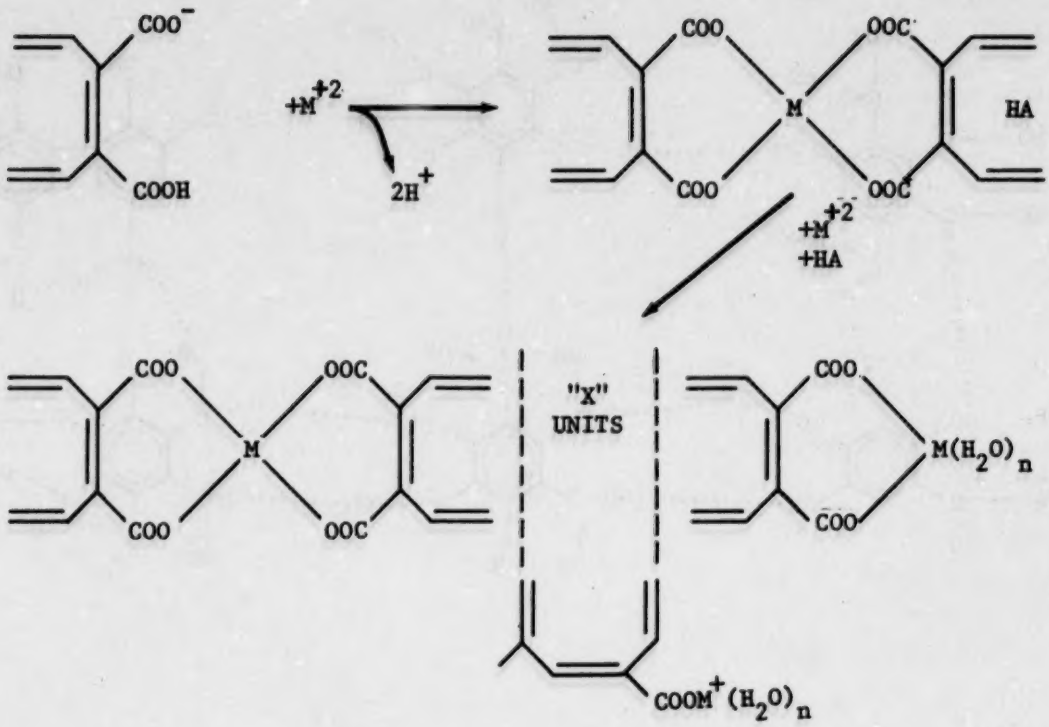
Constituent	Concentration mg/L
Volatile:	
Carbon tetrachloride	Detected but not measured
Benzene	
Toluene	
Xylene	
Methanol	
Ethanol	
Propanol	
2-Butanol	
2-Pentanol	
2-Hexanol	
4-Methyl-2-pentanol	
2-Heptanol	
2-Octanol	
Acetic acid	
Propionic acid	
Butyric acid	
Propanamide	
2-Methylethylenimine	
Methylamine	
Methylamine hydrochloride	
Dimethylamine	
n-Propylamine	
Diethylamine	
n-Butylamine	
Di-n-propylamine	
Di-n-butylamine	
n-Hexylamine	
Carbon dioxide	
Hydrogen	
Nitrogen	
Oxygen	
Argon	

Source: Khare and Dondero (1977)



Source: Schnitzer, 1976.

FIGURE 7. A PARTIAL CHEMICAL STRUCTURE FOR FULVIC ACID.



Source: Stevenson, 1976.

FIGURE 8. COMPLEXATION OF A METAL ION BY HUMIC ACID.

Because of the ill defined structure and nature of humic and fulvic acids, their direct effect on complexation in natural leachate is difficult to assess. Furthermore, realistic modeling in a synthetic leachate with a non-polymeric compound will be difficult. Comparison between empirical values of stability constants of fulvic and humic acids and other appropriate ligands, at the very least indicate systems of similar complexing ability and thus may provide better models than systems which are intended to mimic the structure.

Oxidation - Reduction Reactions

Leachate is likely to be highly dynamic, rather than in or near equilibrium conditions, with respect to oxidation-reduction reactions. First, most redox reactions are slow compared to acid-base reactions; and second, microorganisms in leachate may well be the principal mediators of oxidation-reduction reactions under natural conditions. Because the above factors make an exact description of the redox environment of natural leachate impossible, only those factors which define the redox gradients, and significantly affect the transport mechanisms within the leachate will be considered.

Meaningful and direct redox measurements are most difficult to obtain in natural systems. It is possible that many redox environments co-exist in the same landfill or redox couples may be present in varying degrees of completeness depending upon kinetic factors. Before discussing the effect of the redox environment on species transport, it is necessary to establish a working definition of such an environment. Two terms are generally used to describe redox systems, the redox potential, E_H, and the relative electron activity, $p\varepsilon$. Formally, in systems where half reactions are written for the transfer of a single mole of electrons

(22) $$\sum\left(\frac{n_i}{n}\right) A_i + e^- = 0$$

where A_i designates the participating species, n_i their numerical coefficients, positive for reactants and negative for products, and n the number of electrons transferred, $p\varepsilon$ is equal to

(23) $$p\varepsilon = p\varepsilon^\circ + \log\left(\prod [A_i]^{(n_i/n)}\right)$$

and

(24) $$p\varepsilon^\circ = \log K$$

where K is defined by

(25) $$K = \prod [A_i]^{-(n_i/n)}$$

Thus $p\varepsilon$ is an intensity factor and measures, in a manner analogous to acid or base neutralizing capacity with respect to protons, the redox capacity of a given system.

It is also possible to define the redox potential, E_H, of the same system using the Nerst equation

(26)
$$E_H = E^o_H + \frac{2.3\ RT}{nF} \log \quad [A_i]^{n_i}$$

where R is the ideal gas constant, T is the temperature in degrees Kelvin, F is equal to Faradays, and other terms as defined previously. Thus E_H and $p\varepsilon$ are related by

(27)
$$p\varepsilon = \frac{F}{2.3\ RT} E_H$$

Thus far, distribution of various species in leachate have been considered in two ways: (1) equilibria between chemical species in a particular oxidation state as a function of pH and solution composition; and (2) equilibria between chemical species at a particular pH as a function of $p\varepsilon$. Of particular use in consideration of redox environments is a combination of the above as shown in Figure 9, i.e., $p\varepsilon$ - pH stability field diagrams which show how protons and electrons simultaneously shift the equilibria under various conditions and indicate which species predominate under any given condition of $p\varepsilon$ and pH.

Dynamic redox environments in landfills can affect species transport in two ways: (1) by direct changes in the oxidation state of metal ions and/or (2) by redox changes in available and competing ligands. The range of typical redox environments in landfills as found by Chian and DeWalle (1976) are shown in Figure 10.

As previously mentioned, microorganisms act as catalysts for redox reactions; thus, these organisms do not "oxidize" or "reduce" substrates but rather mediate the electron transfer between substrates. Therefore, because their effect is kinetic rather then thermodynamic their influence on leachate generation is particularly difficult to assess. While specific microbial mechanisms of redox control remain elusive, their effects (i.e., shift in the potential) on the redox environment may be considered as the consequence of ligand formation with the original oxidant and products.

Rather than attempt to formulate a complete system (which is an exceedingly complex problem), it is sufficient for the purposes of this document to focus only on the direction and extent of shifts of potential associated with the formation of complexes. Moreover, effects of the system pH on the ligand equilibria are not considered explicitly; such effects may best be evaluated from empirical data at different pH numbers. Thus for the general reaction:

$$O + R \rightleftharpoons \text{Products}$$

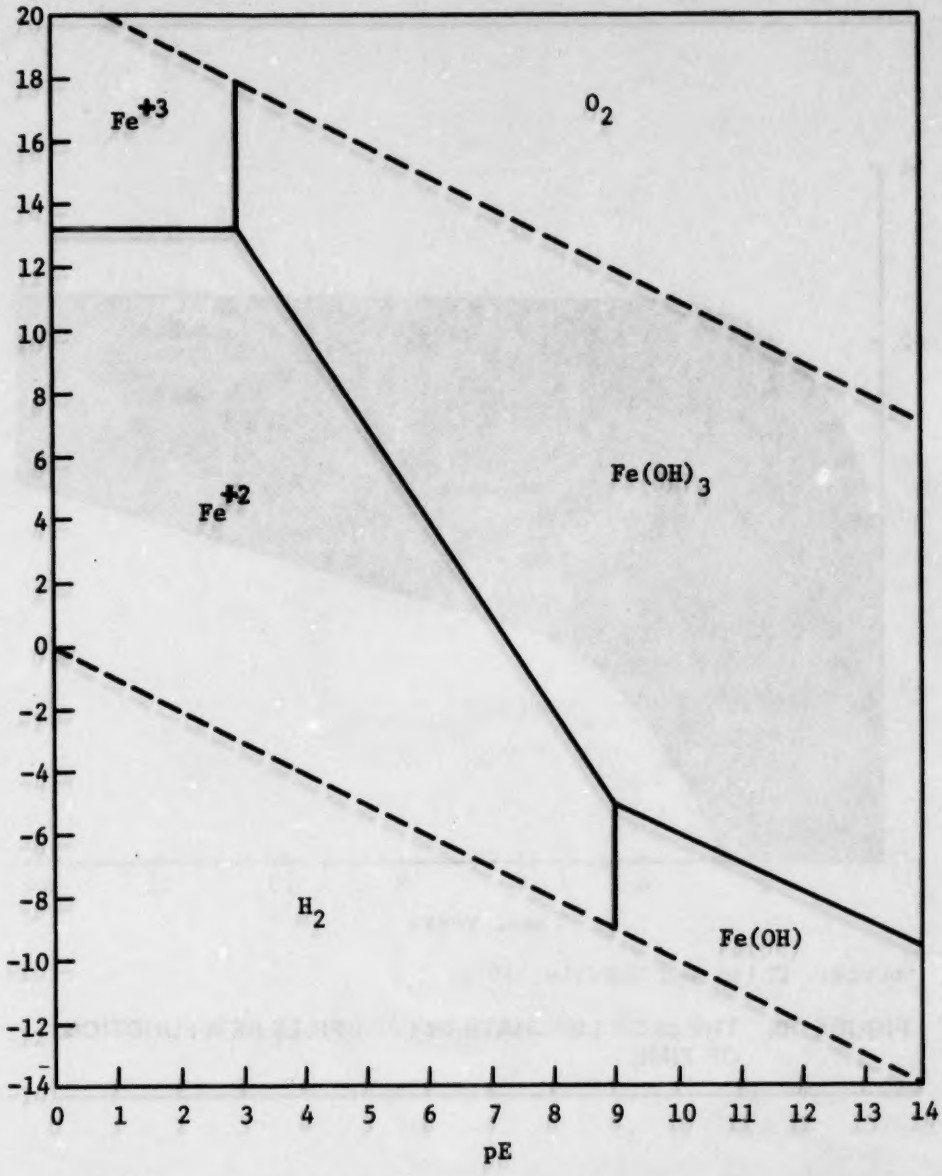
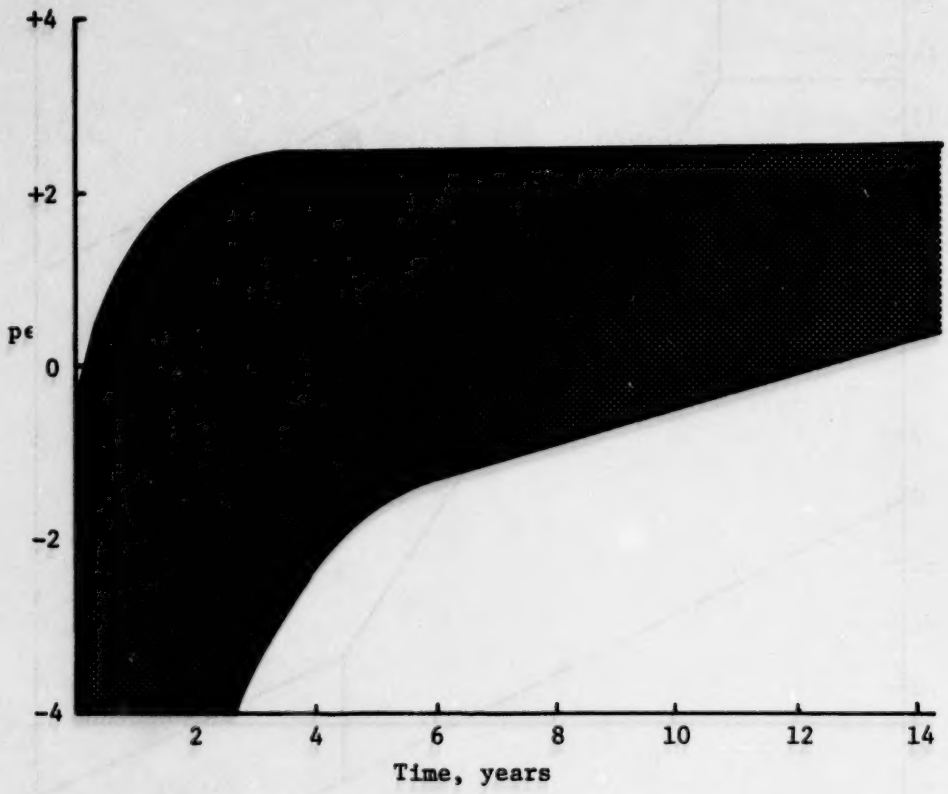


FIGURE 9. SIMPLIFIED pε – pH DIAGRAM FOR IRON IN WATER.



Source: Chian and DeWalle, 1976.

FIGURE 10. THE pε OF LEACHATE IN LANDFILLS AS A FUNCTION OF TIME.

where O and R represent the original oxidant and reductant respectively, the reactions for formation of complexes with O and R and:

$$O + nL \rightleftharpoons OL_n$$

and

$$R + mL \rightleftharpoons RL_m$$

where n and m are the mole numbers. If stepwise formation constants are neglected (or impossible to measure experimentally), the following equilibrium equations may be written:

(28) $$[O][L]^n / [OL_n] = K_o'$$

and

(29) $$[R][L]_m / [RL_m] = K_r'$$

These equations define the degree of complex dissocation and are commonly known as instability constants. It is further useful to define the following sums:

(30) $$S_o = [O] + [OL_n]$$

(31) $$S_r = [R] + [RL_n]$$

(32) $$S = S_o + S_r$$

(33) $$S_L = [L] + n[OL_n] + m[RL_n]$$

In the case where K_o' and K_r' are very large, a further simplification can be made, namely that

(34) $$S_L \cong [L]$$

Even if K_o' and K_r' have very large values, this does not preclude the formation of considerable amounts of a complex at high values of [L]. Using the above equations (28) - (34) to define [O] and [R],

(35) $$[O] = \frac{S_o K_o'}{K_o' + S_L^n}$$

and

(36) $$[R] = \frac{S_r K_r'}{K_r' + S_r^m}$$

and from the Nerst equation (26), then the potential of the system may be expressed as*

$$(37) \qquad E_H = E_H^o + \frac{RT}{NF} \ln \frac{K'_o}{K'_r} + \frac{RT}{NF} \ln \frac{K'_r + S_L^m}{K'_o + S_L^n} + \frac{RT}{NF} \ln \frac{S_o}{S_r}$$

For simplicity it has been further assumed that $m = n$ and $S_o = S_r$. Thus there are three non-trivial cases to consider: (1) $K'_o = K'_r$; (2) $K'_o > K'_r$; and (3) $K'_o < K'_r$.

Case 1. If $K'_o = K'_r$, there will be no shift in the system potential. However, it is important to remember that this may be true only under specific conditions. In particular, recall that pH changes in a system may effect formation constants enormously.

Case 2. If K'_o is greater than K'_r, the ligand binds more tightly to the reductant R, than to the oxidant, O. If $m = n$ the second and third term of equation (37) increase with S_L and approach the value of the second term at high values of S_L. For this limit then,

$$(38) \qquad E_H = E_H^o + \frac{RT}{NF} \ln (K'_o / K'_r)$$

The shift in potential is positive and directly proportional to the ratio of K'_o/K'_r.

Case 3. When K'_r is greater than K'_o then the ligand is more strongly bound to the oxidant than to the reductant. It is unnecessary to repeat the argument given for case 2, except to note that the shift in potential will be negative and reach a limit when O and R are saturated with the ligand.

What systems, then, must be considered in light of the above? The results of Table 6 (cf Table 1) show that iron, and to a lesser extent, zinc

TABLE 6

RANGE OF HEAVY METAL CONCENTRATIONS FOUND IN LEACHATE[1]

Species	Concentration Range mg/L
Fe	0 - 2,820
Zn	0 - 370
Mn	0.1 - 125
Cd	0.03 - 17
Cu	0 - 10
Pb	.1 - 2

Source: Chian and DeWalle (1976)

*For treatment of the generalized system, see Clark (1972) pg. 212-213.

and maganese represent the bulk of heavy metals present in leachate. Due to the reduced conditions present in all but very young or old landfills, soluble metallic species will occur in their reduced states. Thus modelling of any natural leachate system might well include at least the most predominant of these metals, iron (II).

In summary, while oxidation or reduction of chemical species is unlikely to depend solely on a shift of potential, the effects outlined above should be considered when evaluating the redox environment of natural systems. A further point to remember when using empirical data of naturally occurring oxidation-reduction systems is that such data is practically limited to homogeneous environments whereas these systems occur naturally in very heterogeneous environments.

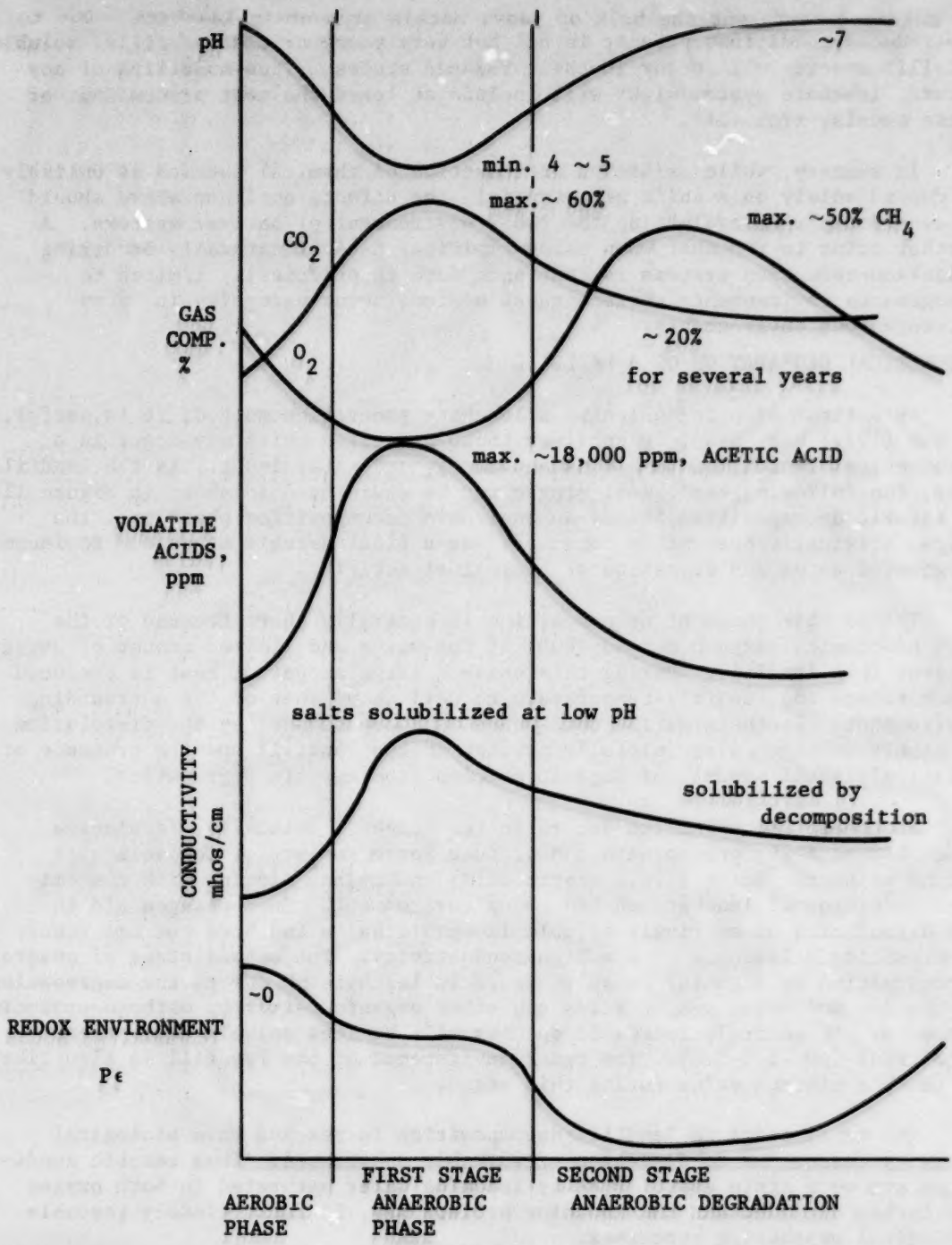
THEORETICAL DEGRADATION OF A LANDFILL

As a first step in designing a leachate generation method, it is useful, as Ham (1977) has done, to consider those processes which may occur in a hypothetical landfill with a constant energy and water input. As the landfill ages, the following biological stages may be envisioned as shown in Figure 11: an aerobic decomposition phase; an anaerobic decomposition phase once the oxygen originally present is consumed; and a final aerobic stage due to incoming oxygenated water and cessation of biological activity.

The aerobic phase of decomposition is generally short because of the high biochemical oxygen demand (BOD) of the waste and limited amount of oxygen present in a landfill. During this phase a large amount of heat is produced which raises the landfill temperature to well above that of the surrounding environment. Leachate during this phase is characterized by the dissolution of highly soluble salts initially present in the landfill and the presence of relatively small amounts of organic species from aerobic degradation.

Anaerobic decomposition occurs in two stages. Initially, faculative anaerobic bacteria predominate and produce large amounts of low molecular weight aliphatic acids (e.g., acetic acid) and carbon dioxide with concomitant reduction of leachate pH and redox environment. Such changes aid in the dissolution of sparingly soluble inorganic salts and have the net result of producing a leachate with a high conductivity. The second stage of anaerobic decomposition is signaled by an increase in leachate pH due to the degredation of the low molecular weight acids and other organic matter by methane-producing bacteria. In general, inorganic species will be less soluble under these conditions (pH $\simeq$6.6-7.3). The redox environment of the landfill is also likely to reach a minimum value during this stage.

The final stage in landfill decomposition is reached when biological activity ceases due to depletion of suitable substrates. Thus aerobic conditions are once again established by incoming water saturated in both oxygen and carbon dioxide, and the leaching pattern may, in fact, closely resemble geological weathering processes.



Source: Ham et al., 1977.

FIGURE 11. THE THEORETICAL DEGRADATION OF A LANDFILL.

Clearly, environmental conditions can and will alter a theoretical degradation pattern considerably; however of necessity, degradation has been considered to be a constant (i.e., uneffected by precipitation rate, temperature changes, etc.) and homogeneous process. While these assumptions are gross over simplifications and intended only to provide a framework within which leachate generation may be considered, the trends identified above roughly follow those of natural leachate as shown by Chian and DeWalle (1976, 1977) in Table 7. The only significant deviation is that of the redox potential, which from their data reaches a minimum value early in the life of landfill (before two years) and then rises to high levels, paralleling the behavior of pH.

SUMMARY OF RELEVANT TEST PARAMETERS

The determination of specific mechanisms by which organic and inorganic contaminants in solid waste are leached is an exceedingly complex problem; indeed, the preceding sections have only constructed, in the broadest terms, a fremework in which the rudiments of these individual mechanisms have been discussed. More important, however, has been the identification of those parameters (and mechanisms in some cases) which most affect leachate composition.

Clearly, the solubility of inorganic species and coordinative compounds of metal ions is the most important phenomena responsible for the presence of toxic contaminants in leachate. The most important parameters affecting the solubility of inorganic species are (a) the pH of the medium and (b) the type and concentrations of complexing ligands (both organic and inorganic) present. Also important, although much more difficult to conceptually model, is the redox environment of the system. With an understanding of these factors, the overall mechanism of leaching may be theorized.

Of lesser importance are the parameters of temperature and particle size. Temperature changes within the environment of a landfill are most likely to affect the rate of biodegradation. The solubilities of inorganic species as a whole, while certainly a function of temperature, are unlikely to change significantly with the temperature changes found in a landfill. The surface area, or particle size of the waste, should not affect the equilibrium concentrations of species in leachate, although it may have profound affects on the kinetics of leachate generation.

With these concepts and their relative effects thus defined, existing leachate generation procedures may now be considered. These concepts, however, are not rigorous relationships and thus serve only as guidelines for method evaluation.

TABLE 7

RANGE OF LEACHATE COMPOSITION IN SANITARY LANDFILLS IN THE UNITED STATES

Parameter	Concentration[1]
COD	40 - 89,520
BOD	81 - 33,360
TOC	256 - 28,000
pH	3.7 - 8.5
TS	0 - 59,200
TDS	584 - 44,900
TSS	10 - 700
Specific Conductance	2,810 - 16,800
Alkalinity ($CaCO_3$)	0 - 20,850
Hardness ($CaCO_3$)	0 - 22,800
Total P	0 - 130
Ortho-P	6.5 - 85
NH_4-N	0 - 1,106
NO_3+NO_2-N	0.2 - 10.29
Ca	60 - 7,200
Cl	4.7 - 2,467
Na	0 - 7,700
K	28 - 3,770
Sulfate	1 - 1,558
Mn	0.09 - 125
Mg	17 - 15,600
Fe	0 - 2,820
Zn	0 - 370
Cu	0 - 9.9
Cd	0.03 - 17
Pb	<0.10 - 2.0

[1]All figures in milligrams per liter except Specific Conductance which is measured as micromhos per centimeter and pH as pH units.

Source: Chian and DeWalle, 1976

SECTION 3

COMPLIATION AND EVALUATION OF LEACHATE GENERATION METHODS

Using the information from Section 2, realistic criteria for critical evaluation of leachate generation methods may be established. Specifically, the following points will be considered:

- Does the test protocol address test variable in a reproducible manner?
- Are the test conditions relevant to those factors which control leaching in actual landfills? (Severe conditions are not necessarily irrelevant per se, but unnaturally severe conditions (e.g., leaching with a concentrated acid) are to be avoided.)
- How may the test data be interpreted? Do they serve the legislative and regulatory needs of EPA?

In the absence of a quantitative model for leachate generation, any evaluation will be qualitative and, of necessity, somewhat subjective. Furthermore, it is important to note that relatively few of the tests compiled were specifically designed for assessing leachate generation within a landfill.

The compilation of laboratory shake test protocols for leachate generation are presented in Table 8 in the following format:

- Method - Test originator and references
- Variables - Variables addressed by the test
- Description - A concise summary of test procedures
- Advantages, Disadvantages - The relative merits of the tests based on the criteria listed previously
- Remarks - Purpose of the tests as defined by the test originator

TABLE 8 LEACHATE GENERATION METHODS

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Battelle Laboratories (Barton, 1965)	• pH • Liquid to Solid Ratio • Temperature • Particle Size • Test Duration	The following methods have been used for the assessment of radioactive wastes. A sample is crushed and a (approximately) 1 gram sample of -45 + 60 mesh particles is placed in a stainless steel "tea bag". This is suspended in 150 ml distilled water at 95°C. The eluant is changed (and analyzed) at 24 hour intervals.
(Mendel, 1973)		Slow leaching tests have been conducted at Battelle, Pacific Northwest Laboratories in the following manner: Samples are leached at the desired temperature in an especially designed apparatus (Mendel, 1973, pages 25-26). The apparatus is designed to leach one piece samples, although powdered samples may be leached if the sample is supported on sintered glass or contained in a porous bag. The ratio of eluant volume to sample volume is comparatively high in this technique, typically being 100 or greater. Dynamic contact between eluant and solid is maintained by an airlift recirculator. The eluant is changed periodically, usually daily, when the initial leach rate is at a maximum.
EPRI (Weir et al., 1975)	• pH • Buffering Capacity • Liquid to Solid Ratio • Test Duration • Agitation Method	A sample is stirred for 24 hours with deionized water in a closed container at a liquid/solid ratio of 5:1. After filtering with a porous membrane filter, the leachate may be analyzed. The effect of pH is evaluated by varying pH between 7.5 and 13 using a carbonate buffering system. The kinetics of leachate generation may be evaluated using procedures similar to the above. Samples were agitated for 96 hours (to insure equilibrium) and the mixtures were sampled at 2, 5, 10, 60, 480, 1445 and 2880 minutes.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
This method has been relatively well tested and does provide reproducible leach rate data from immobilized radioactive wastes. Kinetic leaching patterns may be estimated from the test data.	The method does not consider the environmental conditions in a landfill. The eluant is distilled water and as such is not representative of natural eluants. The method of Mendel requires complex testing apparatus which is not readily available.	This test is specifically designed to determine the characteristics of the leaching of radioactive materials from immobilized waste solids and is proposed as an accelerated leach test for leach rate determination. There are two principal uses to which the results of leachability measurements on solid wastes are put: (1) Comparison of one method of waste insolubilization with another; and (2) Making estimates of the hazards arising from the contact of a solidified radioactive waste with water under conditions during storage or shipping. Hespe (1971) under the auspices of the International Atomic Energy Agency, has proposed a standard method for leachate generation from solid (immobilized) radioactive wastes. This method is extremely tedious and requires a test period of many weeks.
The effect of pH on leachate generation is considered. Leachate kinetics are addressed by this procedure. The test procedure is relatively simple.	The method does not address the environmental conditions in a landfill. Furthermore the eluant is unrepresentative of natural eluants in a landfill. Equilibrium conditions are not likely to be reached in 24 hours. The liquid to solid ratio is relatively low so that common ion effect may be enhanced with the result that only the most soluble species will leach.	This test has been used for the evaluation of leachate from bottom and precipitator ash. Column sorption tests are performed using these leachates. Relatively small soil columns are used (height 4cm, width 3.5 cm). The columns are attached to a vacuum system which is used to regulate flow.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Federal Republic of Germany (NATO, 1976)	• pH • pε • Buffering Capacity • Liquid to Solid Ratio • Test Duration	Initially the waste is separated into liquid and solid phases by centrifugation or filtration. The solid phase (residue) is mixed with distilled water at a ratio of 1:10. It is then agitated for 24 hours. Conductivity measurements are taken periodically to establish solubility equilibrium. The mixture is filtered and then analyzed for the desired constituents. Additionally the original liquor from centrifugation is analyzed.
Hydro Research Laboratories	• Liquid to Solid Ratio • Test Duration • Agitation Method	Dredged material and unfiltered composite disposal site water are mixed in a 1:4 volumetric ratio. This is done by placing 100 ml of water in a 2000 ml graduated Erlenmeyer flask, carefully adding dredged material until the mixture reaches 300 ml, and filling the flask to 1000 ml with water. The flask is stoppered with a polyethylene stopper and shaken virgorously for 30 minutes on a mechanical shaker. The suspension is then carefully decanted, centrifuged, and filtered through a 0.45 membrane filter. The elutriate is stored in clean polyethylene bottles.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
Effects such as pH, buffering capacity, and $p\epsilon$ are considered. An attempt is made to determine whether equilibrium conditions are reached. The test procedure is relatively simple.	The method does not address environmental conditions in a landfill specifically. The eluant (i.e., 0.1N HCl, 0.1N NaOH) is unnaturally severe. The liquid to solid ratio may enhance the common ion effect with the result that only the most soluble species will leach. No provision is made for estimation of leachate generation kinetics.	This method is intended primarily to determine soluble chemical species and is not intended to simulate leachate generation per se. The waste may be extracted with fresh eluant to estimate solubilization pattern. The effect of pH may be evaluated by using the following eluants: 0.1N HCl; 0.1N NaOH; and H_2O saturated with CO_2 and O_2.
Environmental conditions at the site of disposal are considered. The test procedure is relatively simple. This method has been extensively used for evaluation of dredged material disposal. Aerobic or anaerobic conditions may be controlled if an appropriate compressed gas is used as a means of agitation.	The test method is designed specifically for dredged material assessment. The liquid to solid ratio is relatively low and thus may enhance the common ion effect.	See entry at Waterways Experimental Station (WES).

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Illinois Platers' Waste Task Force (Illinois Platers' Waste Task Force, 1977)	• pH • Buffering Capacity • Liquid to Solid Ratio • Test Duration • Agitation Method	A quantity R (given by Equation 1) of homogenized sample is taken and added to approximately 1000 ml. of deionized water. The pH of the solution is initially adjusted to pH 5 with 1:1 HCl or 1 N NaOH. pH measurements are to be determined electrometrically following standard calibration procedures. Samples are to be stirred, using an overhead plastic stirrer (stainless steel is acceptable in most instances) or magnetic stirrer for a period of 24 hours $\pm$ 0.5 hours. pH adjustment is to be maintained during leaching within pH 4.9 - 5.2. (1) R = D/3 where R = grams of sample added to one liter of solvent D = density of material to be leached in kg/m^3 1/3 = conversion factor to approximate two years of precipitation pH ADJUSTMENT: The preferred method is a continuous adjustment of pH as a function of time (Procedure A), if the equipment is not available, then (Procedure B) is to be used. PROCEDURE A: If an automatic titration system is available with the capability of preselection of endpoints, or continuous titration to a specific pH such as the Mettler DK 11, DK 10, DV 10, DV 11, or similar systems, then after initial adjustment to pH 5 and calibration as per manufacturer's specifications, the stirred leach is constantly adjusted to pH 5 throughout the 24 hour leaching period. PROCEDURE B: After initial adjustment to pH 5, the pH is readjusted at 15, 30 and 60 minute intervals moving to the next longer interval if the pH adjustment is within pH 5.0 $\pm$ 0.5 during the present interval. This procedure is to be conducted for a minimum of 6 hours. Final pH after a 24 hour interval must be within the range 4.9 - 5.2.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
This test is well controlled with respect to pH and buffering capacity and is generally representative, in terms of the above, of actual environmental conditions. The method attempts to relate the liquid to solid ratio to actual site conditions.	The eluant, as a whole, is unrepresentative of natural eluants. Equilibrium conditions are unlikely to be reached in 24 hours. The liquid to solid ratio is likely to enhance common ion effects. This test method is relatively complex. Environmental conditions, other than precipitation rate, are not considered.	This test has been unanimously adopted by the Illinois Platers Waste Task Force. This procedure is acceptable to the landfill industry representatives, the electroplating industry representatives, and the Illinois regulatory agency representatives when used as a pre-disposal, reproducible analytical standard for the laboratory determination of waste characteristics.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
International Atomic Energy Agency (Hespe, 1971)	• pH • Liquid to Solid Ratio • Temperature • Particle Size • Test Duration	The following procedure has been summarized from the proposed test protocol: The sampling container is a 5 - cm diameter cylinder x 5 cm in height open at one end. Samples are cast in the leaching container, subsequently removed from the container and coated on all surfaces but the top with a waterproof compound which will adhere strongly to the specimen surface. The sample is leached in a suitable inert container under the following conditions: Sufficient eluant (distilled, deionized water) is added to ensure that a layer of solution at least 5 cm deep on stands above the exposed surface of the specimen. The eluant is added accurately measured and is such that the value of the ratio $\frac{\text{volume of leaching solution}}{\text{exposed area of sample}}$ does not exceed 10 cm.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
This method has been relatively well tested and does provide reporducible leach rate data from immobilized radioactive solid wastes. Data from such tests has been successfully extrapolated to transport modeling studies.	The method does not consider those environmental factors which are relevant to solid waste disposal in a landfill. The eluant (distilled, deionized water) is not representative of natural eluants. This method is relatively complex and tedious.	This test has been proposed as a standard method for measuring the leach rates of immobilized wastes. As such the specification embraces two test methods: The first, called the "intercomparison method" is intended to provide a firm basis for the various intercomparisons which have been found to be necessary in this field, i.e., between laboratories, processes, etc. It is suitable for the immobilizing materials (cement, bitumen, plastic, glass) which have been used up till now. The second is called the "environmental method." Since it is impossible to reproduce, in the laboratory, the conditions likely to be met in the field, this method will not predict the precise performance of a waste solid under the conditions of the disposal environment. It will, however, provide the information necessary for a reasonably realistic hazards assessment of a proposed "waste solids-environment" system. The results shall be expressed by a plot of the cumulative fraction of radioactivity leached from the specimen as a function of the total time of leaching thus $\frac{\Sigma a_n}{A_o} \Big/ \frac{F}{V}$ versus Σt_n $\frac{\Sigma a_n}{A_o}$ versus $\Sigma\sqrt{t_n}$ where a_n = radioactivity leached during the leachant renewal period. A_o = radioactivity initially present in specimen. F = exposed surface area of specimen (cm^2). V = volume of specimen (cm^3). t_n = duration (days) of leachant renewal period.

The results may also be expressed by a plot of the incremental leaching rate, R_n, as a function of the time, t (days) of leaching, where $R_n = a_n/A_o \Big/ (F/V)t_n$ and the other terms are as defined above (23). Values for R_n, calculated as above, shall be plotted against t_n-$(t_n - t_{n-1})/2$.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
IU Conversion Systems (IUCS, 1977)	• Liquid to Solid Ratio • Test Duration • Agitation Method • Particle Size	From the material to be tested which is at the moisture content present or anticipated in the field, select a representative sample for testing equal to an amount approximately twice that required for the shake test. When simulating an actual field placement of stabilized soil or waste material, the relative density and permeability coefficient of the material should be known so that these values can be compared to the actual field values. ASTM D2049 and D2434 give methods for determining relative density of cohesionless soils and permeability coefficient of granular soils. A small portion of the sample is reserved for water content determinations according to ASTM standard D2216. (In the case of waste materials containing components with water of hydration, the drying temperature should be modified to 37.8°C (100°F)± 1°C (1.8°F) to avoid removing any water of hydration during moisture content determinations.) A total of 6 samples are taken, five of which weigh 125g ± 13g (dry weight) and one weighing 500g ± 50g (dry weight). In the case of monolithic stabilized soils or waste materials, the samples should be circular slices from a standard Proctor or 3" x 6" cylinder. All samples are leached in sealed polyethylene containers of at least 3000 ml capacity at a 4:1 liquid to solid ratio (eluant as defined in point (2) under remarks) using a recipricating shaker set at an oscillation rate of 60 to 70 one inch strokes per minute. The five 125g samples are agitated for 1, 2, 4, 8, and 24 hours respectively. At the end of each agitation period the mixture is vacuum filtered using a 0.45μ membrane filter. The 500g sample is agitated for 48 hours. After allowing this test specimen to settle for 5 minutes, a suitable portion of the supernatant is removed for determination of particulate and dissolved matter in accordance with ASTM method D1888. The remaining mixture is filtered as above. The leachate thus obtained is analyzed for the desired chemical constituents.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
This method has been extensively used (by IUCS) to determine the leachability of a large number of immobilized industrial wastes. This method has been proposed by ASTM as a tentative method for leachate assessment. This method seeks to model natural leaching conditions by using the natural eluant and using the waste in the physical form in which it is likely to be disposed (e.g., the surface are and permeability of the sample are not modified). Leachate kinetics may be estimated from this method. Equilibrium conditions are more likely to be reached in 48 hours.	Water specific to the field site (or Type II reagent water certainly) will not be representative of eluants in a landfill The liquid to solid ratio is such that common ion effects may be enhanced and thus only the most soluble species will be leached in this test. Conditions within a landfill (e.g. aerobic or anaerobic conditions) are not addressed by this test.	This method covers the determination of both the surface washing and the long-term diffusion-controlled leachate properties of a soil or waste material. It is applicable to all solid and semi-solid materials. The procedure is to establish representative values of the surface washing and the long-term diffusion-controlled leachate properties of a soil or waste material as placed in embankments, landfills, and other disposal or use sites. Such values can be used in the evaluation of the environmental impact of disposal or use sites. As tested these properties result from prolonged water contact both on the surface of the soil or waste materials and on a portion of the interior of a mass of soil or waste material as limited by the permeability of the material. In an actual site prolonged water contact may not be the primary leaching mechanism. The data derived from this procedure should be carefully interpreted with this fact in mind. The following test conditions are prerequisites: (1) continuity of water movement during test with constant rate of water movement; (2) the water used in the test shall be representative of water specific for the field site or Type II grade reagent water as defined by ASTM standard D1193; (3) the relative density and permeability of soil or waste material evaluated in test should approximate the relative density and permeability of the soil or waste material as placed or as anticipated in the field site; and (4) the dry weight of the test speciment plus the volume of the water used in the test must be known accurately.

The six leachate samples are chemically analyzed by the appropriate ASTM method for the following parameters: pH, alkalinity (total and phenolphthalein), hardness, total dissolved solids, total suspended solids, SO_3^{-2}, SO_4^{-2}, Cl^-, As, Ca, Cd, Cr, Cu, Fe, Hg, Mn, Na, Pb, Zn. It is suggested that 1, 2, 4, 8 and 24 hour samples be analyzed at a minimum for pH and total dissolved solids. The 48 hour sample should be analyzed for all parameters.

TABLE 8 (CONTINUED)

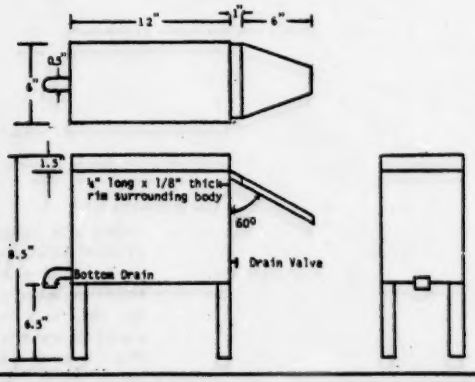
METHOD	VARIABLES ADDRESSED	DESCRIPTION
IU Conversion Systems, Surface Runoff Test	• Liquid to Solid Ratio (V/V) • Test Duration	A representative sample (of which a small portion is reserved for moisture determination) is taken as above. A test box (see below) with dry standard sand (ASTM C778) to a depth of 2" and weighed. The waste material is placed in the box in uniform layers in simulation of actual site conditions, i.e., the moisture and relative density of the material in the box should simulate that of the field site. For material which will be compacted in the field, 3 equal layers of waste material are compacted to the desired density successively with a manual rammer. The slope of the waste material is adjusted to simulate the landfill construction practice (a 1.5% slope is suggested) by placing a shim beneath the rear legs of the test box. One gallon of water, either specific to the field site or type II reagent water (ASTM 1193) is sprayed over the waste at 20 gallons per hour. A clear bucket is used to collect the runoff which is recirculated to the sprayer. Both runoff and seepage/permeate may be analyzed as outlined in the IUCS shake test. The flow rate of 20 gallons per hour corresponds to the following linear feed of surface runoff at the specified rainfall rates rates: Rainfall (in/hr) — Linear Feet of Runoff ¼ — 255 ½ — 130 1 — 65 2 — 35 

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
Surface runoff is measured by this test. This method has been extensively used (by IDCS) to determine the leachability of large numbers of immobilized wastes. This method seeks to model natural leaching conditions by using eluant and the waste in the physical form in which it is likely to be disposed of (e.g., the surface area and permeability of the sample are not modified).	This test while probably be useful to estimate the quantity and quality of surface runoff, does not address the conditions which are found in landfills. Thus, in terms of leachate, relatively little information is provided by this test other than quantity and the gross character of leachate as determined by the most soluble constituents.	This method covers the determination of the surface runoff properties of soil or waste materials. The procedure is to establish representative values of the surface runoff, water absorption, and permeate properties of soils and waste materials as placed in embankments, landfills, or other suitable disposal sites. The following test conditions are prerequisites for suitable simulatef field leaching of soil or waste material to simulate field conditions in as representative and uniform a manner as possible: (1) Continuity of water flow during test, with continuous recirculation of the resultant runoff; (2) Slope of top surface of material in test apparatus shall approximate that present in existing or anticipated field placement of the soil or waste material; (3) Water used in test shall be representative of rainfall at field site or Type II grade reagent water as defined by ASTM standard D1193; (4) Application rate in test shall be representative of rainfall rate at the field site; and (5) Placement of soil or waste material in apparatus shall approximate placement of the soil or waste material in the embankment, landfill, or other suitable disposal site. This procedure may also be used to evaluate the effect of ground water contact with the bottom of the sample by saturating the sample for 7 days. This test can be modified to suit a number of conditions. For example, the test can be run on as-received samples and/or samples cured for various times, as desired. Another alternative is to repeat exposure to a cured sample at regular intervals. Each of these alternatives may be analyzed using approximations and appropriate diffusion equations to give some idea of the rate of mass transport away from the soil or waste material

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Japan Environmental Protection Agency	• pH • Temperature • Test Duration • Agitation Method • Liquid to Solid Ratio	Untreated sludges or solids are mixed with pure water in a ratio of 1:10 (volumetric basis). A maximum of 100 ml is prepared. Neutralizing agents (e.g., HCl, CO_2, NaOH) are added to adjust the pH between 5.8 and 6.3. The solution is shaken or stirred for 6 hours under ambient conditions (temperature and pressure). Solution is then filtered through filter paper type 5-C and centrifuged at 5000 rpm for 20 minutes and analyzed.
State of Delaware	• pH • Liquid to Solid Ratio • Temperature • Test Duration	The sample is leached as received (wet sample) with 25 weights of water per dry weight of sample (this means adding an amount which will increase the water content already in the sludge to 25 times that of the dry weight of the samples. Three portions of the sample are to be treated in this manner, each with the pH adjusted to pH 4, 7, and 10. These three solutions should be mixed overnight in a beaker agitated with a magnetic stirrer at 25-27°C. Filter the three leachate solutions from the solid and analyze using procedures further defined in the U.S. Environmental Protection Agency Manual of Methods for Chemical Analysis of Water and Wastes (1974).

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The effect of pH on leachate generation is considered. The test procedure is relatively simple.	Neutralization with HCl or NaOH may head to excessive dissolution of the waste. The eluant is not representative of natural eluants. Environmental conditions of disposal site are not considered.	This method is used for the evaluation of disposal of solid wastes in fills not near the sea. If the evaluation of disposal sites near the ocean is necessary or desired, the pH of the eluant is adjusted to the range of pH 7.8 - 8.3.
The effect of pH on leachate generation is considered. The high liquid to solid ratio is likely to minimize common ion effects. The test procedure is relatively simple.	The eluant composition is unspecified. The test duration is unspecified.	This procedure is used to evaluate sludge waste materials. The moisture content of the sample is first determined by the following procedure: (1) Weighing the sample as received. (2) Heating it to 103°C to drive off moisture. (3) Re-weighing the sample to constant weight.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Sandia Laboratories (Lynch, 1977)	• pH • Liquid to Solid Ratio	The instantaneous leach test consists of placing a crushed sample (not screened) into a 25-ml Royal Berlin Porcelain filter crucible with a porous bottom, with an average pore size of 7 μm, and pouring 100 ml of deionized water through with the aid of suction. Sample sizes of 1 g or less are used, and flow is adjusted to give water contact times of 3 to 4 min. Weight loss is determined on the sample, and AAS is used to analyze the leachate. The samples are dried for 1 h at 110°C and cooled in a desiccator for 0.5 h prior to weighing. A complete set of data can be obtained within 4 h depending on the number of elements analyzed for in the leachate. The results are typically expressed as grams of a given element leached per gram of sample, e.g. grams of cesium leached per gram of sample. The results can also be expressed as the fraction of an element leached from the sample.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure is rapid and simple. Moreover, test results have shown the test to encompass a wide range of leachabilities with reasonable reproducibility. Common ion effects will be minimized at high liquid to solid ratios.	The method does not consider the environmental conditions in a landfill. The eluant is deionized water and as such is not representative of natural eluants. Equilibrium conditions will not be reached within 3 to 4 minutes.	During the course of the Sandia program for solidification and consolidation of liquid radioactive waste by ion exchange with a hydrated titanate complex, a large number of samples were generated. The leach test proved to be the most time-consuming step in the evaluation of the various samples. By experimenting with various exposure times, it became apparent that in the case of crushed or powder samples, measurable leaching took place in a very short time. Those observations and the advantage of having a test of short duration led to the development of the instantaneous leach test. The instantaneous leach test has proven to be surprisingly reproducible, considering that no attempt is made to control or determine the surface area of the sample. The scatter in the results are well within the acceptable error for measurements of this type. It must be emphasized that the instantaneous leach test reveals nothing of the long-term or high temperature behavior of a sample, which can be varied and complex. Also, due to the randomness of the sample and unknown surface areas, the data are not comparable to those of Hespe or any other standard leach test. However, the test has proven to be a highly reliable, self-consistent means for quickly screening and order ranking materials in a development program. Candidate materials can then be subjected to the more exhaustive, longer time leach tests.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
State of Illinois Environmental Protection Agency Method 1	• pH • Liquid to Solid Ratio • Test Duration	All solid or semi-solid special wastes should be prepared for analysis by leaching with deionized water adjusted to a pH of 6.0 (W/HCl or NaOH). The supernate should be filtered (#40 Whatman) and analyzed. A pre-determined mass of solid sample is added to one liter of water and agitated for 48 hours. Extremely moist samples should have excess liquid decanted prior to leaching, but the sample should not be oven dried. The mass of leached sample is determined from the following relationship: $R = 5.34D$. Where: R = mix ratio of solid sample to water as measured in grams of sample added to a liter of deionized water. D = Density of sample as measured in lbs. per $ft.^3$.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The effect of pH on leachate generation is considered. The liquid to solid ratio is related to the precipitation rate of the intended disposal site. The test procedure is relatively simple. Equilibrium conditions are more likely to be reached in 48 hours.	The eluant is not representative of natural eluants. The relatively low liquid to solid ratio may enhance common ion effects. Environmental conditions within a landfill are not addressed	This method is proposed for use with special wastes (liquid, sludges, and hazardous or potentially hazardous waste). NOTE: If a solid/semi-solid waste (i.e., sludge) is intended for land spreading, the supernatant should be analyzed for both dissolved and suspended components. Thus, the leached supernatant is split into two samples, only one of which is to be filtered. 5.34 is a conversion factor. The mix ratio can be equated to three cubic feet of liquid leached through one cubic foot of solids. (i.e., "36" precipitation/yr.) Results so obtained are considered to be only an approximation of reality. The factors of runoff, evapotranspiration, and the effect of time are not considered in the test but might be logically applied in interpreting these results.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Method 2 Division of Land Pollution	• pH • Test Duration	Enough distilled water is added to a 1/2 gallon sample of the waste solid to fully saturate the contents of each bottle (in the case of fly ash, this amounted to about one liter per sample). The sample is allowed to sit for 24 hours. The supernatant liquid is poured off. A. If the supernatant is sufficiently clear, chemical analysis of the unaltered leachate is conducted. B. If the supernatant is clouded and appears to contain relatively large amounts of suspended and colloidal material, the supernatant is filtered thru Whatman #42 filter paper and is then allowed to sit undisturbed for three days; the supernatant is then poured off and analyzed as above. The supernatant should be analyzed for Ca, SO_4 and heavy metals.
State of Indiana Division of Land Pollution (Lamm, 1977)	• Liquid to Solid Ratio • Temperature • Test Duration	A 20 gm sample is placed in 1 liter distilled deionized water and stirred at room temperature (20°C) for 2 hours using a gang stirrer. The contents are then filtered through #40 Whatman filter paper.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure is extremely simple.	The eluant is not representative of natural eluants. Environment conditions within a landfill are not addressed. This test is a saturation method and thus will estimate only the amounts of the most soluble species. The test procedure, as written is unlikely to be reproducible	In the Arro version of this test diffused air is used for agitation (providing an aerobic condition). The liquid/solid ratio is progressively increased until a point is reached where the leachate is no longer saturated. This typically occurs at ratios of 10:1 to 20:1. The test duration (for each ratio) is 100 hours. The biodegradability of certain materials (e.g., roof shingles) is tested using this procedure. In this case, a synthetic eluant containing bacteria nutrients is prepared. For materials going to a landfill for the first time, the test is conducted only initially. Certain parameters may be monitored later on using in-ground lysimeters. It should be remembered that each sample is leached with distilled water (pH 7.0) and that, under field conditions, leaching may be accelerated and intensified by rainfall, which tends to be acidic, If the waste is being considered for final cover or to be mixed with earth for final cover, test plots of the material should be seeded to determine if the material will support a ground cover.
The test procedure is extremely simple. The high liquid to solid ratio is likely to minimize common ion effects.	The eluant is unrepresentative of natural eluants. Environmental conditions within a landfill are not addresse Equilibrium is not likely to be reached in two hours.	This test has been applied to leachate assessment of combustion residues.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
State of Minnesota, Environmental Protection Agency	• pH • Buffering Capacity • Liquid to Solid Ratio • Test Duration • Agitation Method	A sample of 25 grams is placed in a 2000 ml glass separatory funnel with 1 liter of eluant and vigorously shaken for 60 seconds. (Two eluants have been used: buffered acetic acid solution and distilled deionized water.) The mixture is covered and allowed to stand for 24 hours and then shaken again for 60 seconds. The mixture is now filtered through medium proposity ashless filter paper and the first 10 ml discarded. The acetic acid solution is prepared by adding 49.21 gm HOAc and 39.21 gm NaOAc to enough distilled deionized water to make a 1 liter folution of pH 4.5. The test is conducted at room temperature.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure addresses pH and buffering capacity. The high liquid to solid ratio is likely to minimize common ion effects.	The eluant is not representative of natural eluants. Equilibrium conditions are not likely to be reached in 24 hours. Environmental conditions within a landfill are not addressed. Diffusion effects may control dissolution kinetics (i.e., insufficient agitation of the solution may lead to low results).	This is a test procedure used for evaluating acceptability of most types of industrial wastes for land disposal in a sanitary landfill or in a separate area segregated from refuse deposits. The two eluants used, an acetic acid solution and distilled deionized water, are suggested to approximate conditions in these disposal locations.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
State of New Jersey, Department of Environmental Protection	• pH • Liquid to Solid Ratio • Test Duration	A 500 gram (or otherwise adequate quantity) representative sample is oven dried for 24 hours at 130°C and subsequently stored in a desiccator. A 100 gram portion of the dry sample is added to a solution of 900 ml of distilled, deionized water - acetic acid (sufficient to adjust the pH to between 5.0 - 5.5) of known (i.e., measured) pH and stirred for not less than 24 hours on a multiple-stirring (Phipps-Bird Floc Stirrer) apparatus at 50 rpm. After 24 hours the mixture is vacuum filtered through a fritted glass filter and the filtrate analyzed for the following constituents: Al, As, Ba, Cd, Cr(VI), Cu, Fe, Hg, Mn, Na, N_1, Pb, Se, Zn, Cl^-, CN^-, F^-, ABS/LAS (Surfactants), No_3^-, pH, phenolic compounds (as phenol), oil (soxhlet) extraction, sulfate, TDS, COD, and TOC).

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The effect of pH on leachate generation is considered. The test procedure is straight forward and relatively simple.	The eluant is not representative of natural eluants. Conditions within a landfill are not modelled. The sample is dried and may result in losses of volatile compounds.	This test is recommended for leachate assessment from solid materials intended for disposal in a New Jersey landfill. This leaching test was developed to afford a consistent basis for approving or rejecting various sludge residues destined for landfill disposal. A dried, tared sample added in an approximate ratio of ten percent (by weight) to acidified (acetic acid pH 5) distilled water is suggested to simulate the leachate generated from a sanitary landfill. As the alkaline earth metals and related anions leach out of a residue, the pH would increase to some equilibrium value. This may be construed as similar to the occurrence of alkaline leaching within the landfill itself. The sample is then agitated for 24 hours to provide intimate solid-solution contact which may simulate, to some degree, the flushing action of landfill percolation. Analyses are then performed for general and specific constituents although further data may be in order should the sample contain a specific hazardous material. The characteristics of the leachate are then considered with regards to: 1. Heavy metals (i.e., lead, mercury, cadium, etc.) 2. Toxics (i.e., arsenic, cyanide, selenium, etc.) 3. Organics (i.e., vinyl chloride, PCB, PBB, Phenol, etc.) Although data evaluations are necessarily somewhat subjective, the State of New Jersey attempt to follow, insofar as possible, standard toxilogical limits when formulating final decisions (i.e., LD_{50}, TLV, TLM, etc.). Thus, having both the original residue analysis and leachate characteristics the amount of material leached out over the given period of time may be estimated.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
State of Iowa, Department of Environmental Quality	• pH • Liquid to Solid Ratio • Test Duration	A representative 500 gram sample of the waste is mixed with 3 liters of water and the pH of the solution is adjusted to _____ using _____. This mixture (i.e., water and waste) is shaken periodically over a 24 hour period. The liquid is filtered and the aqueous portion analyzed for the desired parameters. <u>pH Modification Test</u> A representative 500 gram sample of the waste is mixed with 3 liters of water. This mixture (i.e., water and waste) is shaken periodically over a 24 hour period. The pH is determined after 1 hour and 24 hours. If the waste is solid, it should be crushed to a size of approximately 0.5 cm or less.
State of Michigan, Department of Natural Resources	• pH • Liquid to Solid Ratio • Test Duration	A 100 gram sample is mixed with 1 liter of water. The mixture is shaken for 6 hours. The mixture is filtered and the filtrate analyzed for the desired constituents.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The effect of pH on leachate generation is considered. The test procedure is relatively simple.	The eluent composition is unspecified. Test protocol is subject to various interpretations (e.g., what constitutes periodic shaking?).	This leachate test is conducted by the Land Quality Management Division on wastes that are considered to be toxic or hazardous. The pH of the eluent is not specified but rather determined on the waste and disposal site conditions. The parameter to be analyzed is also left blank and depends on the waste.
The test procedure is relatively simple.	The eluent is not representative of natural eluents. The environmental conditions within a landfill are not modelled. Equilibrium is not likely to be reached within 6 hours.	Michigan has attempted to standardize two leachate tests within the past 3 years: a standard leachate test (a column test) and a solubility test (a shake test). A severe leachate test is suggested for materials which would not be disposed of in a licensed landfill. This would include agitation and possible a range of pH of the eluent. The filtrate is then compared to drinking water standards. For those materials which don't pass this test, the waste must be disposed at a landfill with the degree of protection being dependent on the degree of severity of the pollutants in the leachate.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
State of Pennsylvania, Department of Environmental Resources	• Liquid to Solid Ratio • Temperature • Test Duration • Agitation Method	A 500 gram sample (either sludge or filter cake) is added to one liter of distilled water and agitated with a Phippe-Bird stirrer at 60 rpm for 48 hours. The resulting supernate is filtered through #42 Whatman filter paper. Total solids are determined on the filtrate in accordance with Standard Methods (14th edition).
As modified by Bethlehem Steel Corp.	• Liquid to Solid Ratio • Temperature • Test Duration • Particle Size • Agitation Method	A 300 gram sample ground to pass a 10 mesh screen is placed in a 1500 ml beaker; 1000 ml of distilled water are added. The contents are stirred by hand each hour during the workday and allowed to stand at night over a total time period of 4-8 hours. The contents are then vacuum filtered through Whatman #42 filter paper and collected and stored in acid washed glass containers covered with aluminum foil to minimize evaporation. This test is conducted at room temperature (20°C).
State of Texas Water Quality Board	• Liquid to Solid Ratio • Test Duration • Method of Agitation	A 250 gram representative sample of the "dry" material should be taken according to AOAC or ASTM Standard Methods and placed in a 1500 ml Erlenmeyer flask. One liter of deionized or distilled water should be added to the flask and the material stirred mechanically at a low speed for five minutes. Stopper the flask and allow to stand for seven days. Filter the supernatant solution through a 0.45 Micron glass filter. The filtered leachate should be subjected to a quantitative analysis for those component or ionic species determined to be present in the analysis of the waste itself.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure is relatively simple.	The eluant is not representative of natural eluants. Environmental conditions within a landfill are not modelled. The low liquid to solid ratio may enhance common ion effects and thus leaching only the most soluble species.	Initially the Department of Environmental Resources was advocating use of the supernate instead of the filtered supernate. However, that portion of the method was abandoned in favor of filtration because of the dependency of the suspended solids or particulate matter. This test is used to evaluate rain leaching of metallurgical wastes. Samples consisted of blast furnace flue dust, blast furnace slag, BOF slag, BOF dust, electric furnace slag, and electric furnace flue dust.
The test procedure is relatively simple. The reproducibility of the test procedure is considered.	The eluant is not representative of natural eluants. Environmental conditions within a landfill are not modelled. The low liquid to solid ratio may enhance common ion effects thus leaching only the most soluble species.	Triplicate samples of the waste should be leached in order to obtain a representative leachate.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
TRC (Brookman, 1976)	• Liquid to Solid Ratio • Test Duration • Cycles	A weighed portion of the material to be tested is placed in a container with a known volume of distilled water. The resulting mixture is allowed to stand for three days and is then filtered thru a membrane filter (0.45μ). The filtrate is analyzed for species of interest. The media is reweighed and mixed with the same volume of water and the process repeated a number of times. A high liquid to solid ratio (≥10 to 1) is used.
United States Army Corps of Engineers Method 1 (Lee et al., 1975)	• pH • Liquid to Solid Ratio • Test Duration • Agitation Method	A representative sample from the disposal site water column should be collected and analyzed. Sediment samples are taken with a grab sampler or corer and should be representative of the sediment. A mixture of sediment (150 ml) and disposal site water (2850 ml) is placed in a 6 liter Erlenmeyer flask (20:1 liquid to solid ratio). A porous diffusion tube is inserted almost to the bottom of the flask such that the mixture is agitated vigorously by a compressed gas for 30 minutes. The flasks are swirled manually at 10 minute intervals to insure complete mixing. After agitation, the mixture is allowed to sit for 60 minutes and is then filtered (0.45). This electrlate is analyzed for desired constituents.
Method 2 (Malouk et al., 1978)	• pH • pE • Buffering Capacity • Liquid to Solid Ratio • Test Duration • Agitation Method	A 1:4 mixture (by weight) of material and water is prepared. The water used should be saturated prior to the test with CO_2 (pH 4.7). The slurry is then shaken on a wrist action shaker for 1 hour. The sample is centrifuged for 30 minutes at 2500 rpm then filtered using 0.45 filter. The leachate is subsequently analyzed for desired constituents.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure is extremely simple.	The eluant is not representative of natural eluants. Environmental conditions within a landfill are not modelled. Diffusion effects may control dissolution kinetics (i.e., insufficient agitation of the solution.)	Runoff is presumed to be the primary mechanism of waterborne pollutant transport. This test is designed to evaluate leachate potential from material storage piles (e.g., coal, fly ash, etc.) Test data cannot be directly correlated with actual precipitation data, quantity of runoff, and the transport of runoff.
Environmental conditions at the site of disposal are considered. The test procedure is relatively simple. This method has been extensively used for evaluation of dredged material disposal. Aerobic or anaerobic conditions may be controlled if an appropriate compressed gas is used as a means of agitation.	The test method is designed specifically for dredged material assessment. The liquid to solid ratio is relatively small and thus may enhance common ion effects.	This test was designed as a rapid elutriate test for dredged sediments. The test provides information on the chemical compounds released to the water column during disposal of hydraulically dredged material. This test is normally run in triplicate. Aerobic and anaerobic conditions may be simulated by using either oxygen (aerobic) or an inert gas (anaerobic) to mix the samples.
The test procedure considers environmental conditions effecting leachate generation, i.e., pH, p_{O_2}, and buffering capacity. The test procedure is relatively simple.	The eluant is not representative of natural leachate but rather of rainwater. Equilibrium is unlikely to be reached within 1 hour. Environmental conditions within a landfill are not modelled. The liquid to solid ratio is relatively small and thus may enhance common ion effects.	This test was utilized as a rapid leach test for flued and raw FGD sludges.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
United States Environmental Protection Agency		
Method 1 (Statnick, 1976)	• Test Duration • Agitation Method • Cycles	A slurry is prepared using from 2 to 4 parts distilled-deionized water to 1 part solid. This slurry is shaken continuously for 72 hours at room temperature. The slurry is filtered. The above steps are repeated ten times. The leachate from each filtration is analyzed.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure is relatively simple. Leachate generation kinetics may be estimated with this method. Equilibrium is more likely to be reached in 72 hours.	The eluant is not representative of natural eluants. Environmental conditions within a landfill are not modelled. The liquid to solid ratio is small and thus may enhance common ion effects. Repeated leaching with fresh eluant, at least in part, may compensate for this effect.	Mention of this test does not imply current endorsement of this method by EPA. Experience has shown that some species are released immediately from the waste while others are released in the later leachings. The effect of pH on leachability may be determined by adjusting the pH of the slurry to the desired range and following the aforementioned procedures for each pH condition to be evaluated. A similar test has been used by IERL-New Jersey. A liquid to solid ratio of 2.5 is used and samples are agitated for 24 hours using a Burrell Shaker. The Department of Army uses a similar test; liquid to solid ratios of from 4:1 to 1:1 are used. Shake time is 72 hours. The above steps are repeated 7 times.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Method 2 (Abelson and Löwenbach, 1977)	• pH • pε • Buffering Capacity • Temperature • Liquid to Solid Ratio • Test Duration • Cycles • Particle Size • Agitation Method	A 10 gram sample (ground to 100/200 mesh) is shaken with 250 ml of eluant at a constant temperature using a wrist-action shaker set at the maximum rate for 48 hours. The mixture is filtered and both the filtrate and residue are analyzed by appropriate analytical procedures. The eluant should simulate natural conditions. This may be done by saturating distilled, deionized water with carbon dioxide under ambient conditions. (An alternative is the use of plain distilled-deionized water.) The solid to liquid ratio has been arbitrarily set at 25:1; what is important, however, is that species saturation not be reached. Thus, this ratio should be confirmed experimentally and adjusted accordingly, if necessary.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure considers environmental conditions affecting leachate generation, i.e., pH, $p\epsilon$, and buffering capacity. The test procedure, by specifying a high liquid to solid ratio, is likely to minimize common ion effects.	The eluant is not representative of natural leachate but rather of rainwater. Environmental conditions within a landfill are not modelled.	This test has been designed for the environmental assessment of FBC residues. This method is intended to provide a leachate of "worst case" quality. To estimate the quantity of leachate generated the water balance method should be employed (note that the water balance method requires a site survey of topographical, geological, hydrological, climatological, and meteorological conditions.) The following general procedure is proposed: The temperature at which this test is conducted should be selected to represent the mean temperature to which the leached material would be exposed. It should be cautioned that wide variations in test temperature may have an unpredictable effect on leachate quality; certain species (e.g., $CaSO_4$, $CaCO_3$, etc.) are more soluble while others (e.g., $MgCO_3$, $MgSO_4$,) are less soluble as temperature decreases. As part of leachate assessment, the physical properties of test media should be defined. These properties include particle size analysis, specific gravity, bulk density, dry density, water content, porosity/void ratio, and permeability.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
United States Environmental Protection Agency Environmental Monitoring and Support Laboratory (EPA, 1977)	• Liquid to Solid Ratio • Test Duration • Agitation Method	Collect a minimum volume of two gallons of receiving water in a clean glass container with Teflon-covered closure. If it is known in advance that a large number of measurements are to be performed on the dredge mix sample, a 5-gallon sample may be advisable. Analyze the receiving water as quickly as possible for the constituents of interest, using approved analytical procedures. Place a representative portion of the dredge material into a one-liter graduate, filling to the mark. Let the dredge material settle overnight (approximately 16 hours). Carefully decant and discard supernatant. Weigh out 500 $\pm$1 g of the wet, settled dredge material, place in a gallon wide-mouthed jar and add 2 liters of receiving water at room temperature (22°C$\pm$2°). Cap tightly and shake on an automatic shaker at about 100 excursions per minute for 1 hour. At the end of the shaking period remove the jar from the shaker, stand in an upright position and let settle for 1 hour. Carefully decant the supernatant from the settled dredge mix sample into a clean glass container. Analyze for constituents of interest, shaking the sample thoroughly prior to each aliquot removal. Use analytical procedures as stated above. If it appears that the total volume required for all measurements is greater than two liters, proportionately larger weights of dredge material and receiving water may be used. Alternately, several dredge mix-receiving water samples may be prepared, following the above steps, in which case the supernatants should be combined. Calculations: P = S - W, where P = Concentration of Constituent Added to 1 liter of Receiving Water by 250 g of Dredge Material S = Concentration of Constituent in Supernatant from Dredge Mix W = Concentration of Constituent in Receiving Water

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
Environmental conditions at the site of disposal are considered. The test procedure is relatively simple. This method has been extensively used for evaluation of dredged material disposal.	The test method is designed specifically for dredged material disposal. The liquid to solid ratio is relatively small and thus may enhance common ion effects.	This test may be used for assessing the contribution of soluble and partly soluble constituents of dredge materials to receiving water. This test will measure (a) the dissolved materials in the interstitial waters of the dredge material, (b) the readily soluble fractions of the solid phases of the dredge material, and (c) the constituents loosely adsorbed on the solid phases of the dredge material. This test will not measure any of the insoluble or tightly adsorbed material associated with rapidly settleable dredge material.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
University of Wisconsin (Hamm, 1977)	• pH • ps • Buffering Capacity • Organic Constituents • Liquid to Solid Ratio • Test Duration • Cycles • Agitation Method	Samples are first separated into a liquid and solid phase by pressure filtration under an inert gas (e.g., N_2) using a 142 mm 0.45μ glass filter. Some samples, particularly ones containing fibrous materials (e.g., paper, cloth) may require filtration through a wire or plastic screen prior to pressure filtration. Solids collected in this step are combined with those of the second. The resulting filtrate (if present) is analyzed for parameters of interest. A 28.6 gram sample (ground only to the extent necessary to place the sample in the container) is mixed with 200 ml of eluant (1:7 ratio by weight - see below) in a closed container and mixed (rotating shaker (Knabe, 1976)) for 24 hours. The mixture is then filtered through a 0.45μ filter. 200 ml of fresh eluant is added to filtered solid and the process repeated while the filtrate is analyzed for the parameters of interest. The solid is leached a total of three times with fresh eluant over a three day period. No effort is made to control the temperature under which the solid is extracted (other than ambient laboratory conditions). Eluant Composition 0.15M Acetic Acid 0.15M Sodium Acetate 0.05M Glycine 0.024M Iron (II) Sulfate 0.008M Pyrogallol

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
This test is likely to yield the most accurate representation of leachate generation to date. The pH, p_ϵ, and buffering capacity of the eluant are all similar to that found in natural leachate. Test results from this procedure should be interpretable in terms of actual leaching characteristics in a landfill. The test procedure is relatively simple and straight forward; as such the test may be performed in a laboratory with minimal facilities. Kinetic leaching patterns may be estimated from this test.	Equilibrium conditions are not likely to be reached in 24 hours. The eluant is relatively complex and unstable (i.e., eluant probably cannot be stored for more than 1 week). The eluant is toxic and thus, if bioassay methods are used to determine the hazard of the leachate, interpretation of test results may be difficult. The relatively low liquid to solid ratio will probably enhance common ion effects and thus only relatively soluble species may be leached. The organic complexing capacity of this eluant is several orders of magnitude greater than that of natural leachate; furthermore, pyrogallol is not representative of organic constituents commonly found in landfills.	This test has been designed by the University of Wisconsin under EPA Grant No. R804773010. Mention of this test does not imply current endorsement of this method by EPA. This test is specifically designed to evaluate the environmental effects of solid waste disposal in a landfill. As such the following parameters are suggested to be of particular importance in leachate generation: pH, complexing capacity, redox environment, water-immiscible organic solubilizing power, and ionic strength. The landfill degradation processes affecting these parameters were studied, their maximum concentrations determined, and compounds were chosen to model the above parameters. This synthetic eluant will be compared with actual leachate to determine the utility of this method.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Westinghouse Research Laboratories (Kesirns et al., 1975)	• Liquid to Solid Ratio • Test Duration • Agitation Method	Deionized water (250 ml) is mixed with the spent sorbent (25 g) in a 500 ml flask. The mixture is agitated for 24 hours using an automatic shaker (Eberbach) at 70 excursions per minute at room temperature. This supernatant is filtered (Whatman #42 paper) and the filtrate analyzed. This test has been conducted with samples as received and with samples which are finely ground. Shaking may be conducted under aerobic (air atmosphere) or anaerobic conditions (inert atmosphere). Shaking versus non shaking procedures have been evaluated.

TABLE 8 (CONTINUED)

ADVANTAGES	DISADVANTAGES	REMARKS
The test procedure is relatively simple. Aerobic and anaerobic conditions are addressed by this procedure.	The eluant is not representative of natural eluants. Environmental conditions within a landfill are not modelled. Equilibrium conditions are not likely to be reached within 24 hours.	This test has been used as a rapid test for the evaluation of waterborne pollutant release from FBC spent sorbent. This test has been applied to residues from pressurized and atmospheric FBC units (PER, Westinghouse and Esso Miniplant units). Similar test results were obtained despite variations in media surface area (i.e., grinding of the sample prior to shake test) and reaction conditions (aerobic and anaerobic atmospheres). Leachates are analyzed for 31 trace elements, pH, specific conductance, and sulfate. The following was determined from leach tests on spent FBC residue: (1) Calcium and sulfate dissolution plateaued at concentrations limited by calcium sulfate solubility; (2) The equilibrium calcium and sulfate concentrations were high and exceed current water quality criteria; (3) There was negligible dissolution of magnesium species; (4) Insignificant amounts of heavy metal ions were leached; (5) The leachates were alkaline (pH 10.6 - 12.1). Runoff leachates (similar to a column test) show a gradual decrease in pH with the amount of eluant.

TABLE 8 (CONTINUED)

METHOD	VARIABLES ADDRESSED	DESCRIPTION
Roy F. Weston, Inc. (Roy F. Weston, Inc., 1974)	• pH • Liquid to Solid Ratio • Test Duration • Agitation Method	The coal sample is shaken with three solutions an acidic solution (pH 3.9), a neutral solution (pH 7.1), and a basic solution (pH 10). The procedure is as follows: (1) Samples are dried to a constant weight at 105°C. (2) Twenty grams of the sample are placed in 100 ml of water and the pH adjusted to the desired value (HCl and NaOH are used). (3) The mixture is then transferred to a shaker table, which is set at the maximum shake rate for 30 minutes. (4) The supernatant is filtered and the filtrate analyzed for the desired constituents.

TABLE 8 (CONCLUDED)

ADVANTAGES	DISADVANTAGES	REMARKS
The effect of pH on leachate generation is considered. The test procedure is relatively simple.	The eluant is not representative of natural eluants. Environmental conditions within a landfill are not modelled. Equilibrium conditions are not likely to be reached within 30 minutes.	This test has been used to assess the environmental impact of leachate generation from coal piles. The results from the test are suggested to represent worst case levels of leachate quality. The results of these shake tests for coal from the Decker Coal Mine are as follows: (1) Acidic conditions - initial pH 3.9 final pH 9. Heavy metal concentrations were negligible (well below proposed EPA standards in 1973). (2) Neutral conditions - initial pH 7.1 final pH 8.5. Again heavy metal concentrations were negligible. (3) Basic conditions: initial pH 10.0, final pH 9.4. Heavy metal concentrations were negligible.

SECTION 4

SUMMARY AND CONCLUSIONS

The selection or design of any leachate test will ultimately be decided by a number of practical, rather than theoretical, considerations. It must be recognized at the outset, however, that a single test will not be optimal for all wastes. Nevertheless, from a regulatory point of view, developing different tests for each different waste is clearly impractical and probably unworkable.

Any evaluation of a test must first be reproducible and second provide for the rapid assessment of the generation of aqueous toxic contaminants from the disposal of solid wastes in a landfill. Moreover, the particular method of hazard evaluation (e.g., direct measurement of a parameter or a biological assay procedure) must be consistent with the leachate test protocol chosen. Whatever the method of leachate assessment, it is useful to consider what information might theoretically be derived from such tests.

INTERPRETATION OF SHAKE TESTS

Shake tests, the most ambitious of which seek to model those processes which are thought to occur in a landfill, are by definition batch tests. As such, these tests have been designed to yield "equilibria" (or in the case where a solid is leached repeatedly with fresh eluant, a series of "equilibria") rather than kinetic data. Leachate generation under natural conditions, in contrast, is a highly dynamic process rather than a static one. Furthermore, the specific character of leachate, in terms of both quality and quantity, will be site specific.

To a certain extent, these problems may be overcome by proper test design, but a fundamental question remains unanswered: Which stage of leachate generation shall be simulated? Shall the test be designed as a "worst case"* or shall the test be designed to represent a more realistic case, and thus, not maximize pollutant release? The answers to these questions will largely determine the composition of the eluant and the physical conditions under which the test is conducted. Presumably the most active phases of a landfill have the greatest environmental impact and therefore the eluant composition during this stage should be modelled. Thus, by proper choice of parameters, a shake test may be designed to yield information which then may be used to estimate pollutant release rates under natural conditions.

*"Worst case" is defined to be that case in which pollutant release is maximized within the bounds of naturally occurring conditions.

The effect of eluant composition has been previously discussed in detail in Section 2. The most significant parameters in terms of leachate generation have been shown to be (1) the pH of the eluant, (2) the ratio of eluant to waste, and (3) the redox environment of the waste. Because a "worst case" evaluation is generally more useful as a preliminary test, eluant pH should model the most active phase of landfill degradation, i.e., a pH of four to five. Furthermore, the eluant should be well buffered in simulation of natural conditions. To insure that all important species solubilize, the ratio of eluant to waste should be large enough to minimize common ion effects. For insoluble wastes, a ratio of 10 to 20:1 is presumed to be sufficient but should be verified experimentally. Finally, the redox environment should be considered. At this time, however, the specific processes which control this environment are poorly understood. Thus, it is recommended that this modelling be limited to the maintenance of an anaerobic environment by the simple exclusion of air. This may be done by either conducting the entire test in an inert atmosphere (e.g., a dry box filled with nitrogen) or by agitation with an inert gas such as nitrogen.

A principal concern of any test procedure is that of reproducibility; also related to this is the comparability of test results from different wastes. The only method of ensuring that both of these requirements are met is to allow sufficient time for the system to reach equilibrium, which by definition is a unique state of any system examined. Furthermore, if the time to reach equilibrium is considered, equilibrium concentrations may be related to the kinetic leaching pattern within a landfill. However, attainment of equilibrium condicions may require excessive amounts of time (years or longer). Thus, a more reasonable goal is to reach at least a psuedo-equilibrium condition.* Because initially, surface reactions are probably rate controlling, the overall reaction rate (and thus the time needed to reach equilibrium) increases with the surface area of the solid; thus, ideally, the surface area of the waste should be maximized. However, such a procedure may not be practical for all wastes (e.g., a tar or other semi-solid waste).

A fundamentally different approach, and more useful from a theoretical viewpoint, is to obtain kinetic information directly; however, such an approach would require significant analytical effort. The major advantage of a kinetic study is the acquisition of data, such as the effective diffusivity and dissolution rate constant for relevant species, which allows for direct comparison of several wastes. Coupled with solutions of mass transport equations, such data provide a way to estimate the amount of material leached from a landfill as a function of time, taking into account actual site conditions. A major disadvantage, however, is the analytical cost of such a study.

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*Psuedo-equilibrium is defined as a steady-state under controlled redox conditions.

RECOMMENDED TESTS FOR FURTHER EVALUATION

Three tests are recommended for further evaluation: the IUCS shake test; the State of Minnesota shake test; and the University of Wisconsin shake test. These tests were chosen for the following reasons: (1) each test is well written and likely to be reproducible if properly conducted; (2) the tests chosen are exemplary and range from simple to complex (on the basis of eluant composition) protocols; and (3) each test has been specifically designed to assess the environmental impact of solid waste disposal. Yet each test has fundamental differences which suggest further evaluation.

The IUCS test is perhaps the simplest of the tests. In seeking to model natural conditions, water specific to the field site is used as an eluant. Should such water not be available, Type II reagent water is used. The waste is leached in the physical form in which it is likely to be disposed (i.e., the surface area and permeability of the waste are not modified by grinding). Furthermore, this method has been extensively used (by IUCS) to determine the leachability of a large number of industrial wastes. Disadvantages of this test include the low eluant to waste ratio (i.e., common ion effects may be important at a liquid to solid ratio of 4:1) and the lack of modelling of the redox environment. This test has also been considered as a tentative standard by ASTM.

A test of intermediate complexity, the State of Minnesota procedure seeks to model the acidic, highly buffered, nature of leachate. The high liquid to solid ratio 40:1 should minimize any common ion effects. Disadvantages include the short duration of the test (a steady-state condition may not be reached in 24 hours) and the lack of modelling of natural redox considerations.

The most complex and comprehensive protocol is the University of Wisconsin test. Each of the parameters addressed in Section 2 of this document is addressed in some manner by this test. The eluant pH and buffering capacity is modelled after natural leachate. The redox potential, together with the complexing ability of the eluant, are addressed by the addition of a pyrogallol-iron (II) complex. The agitation method has been designed to minimize particle attrition during the test. Disadvantages include the short duration of the test (a steady-state condition may not be reached in 24 hours) and the relatively low liquid to solid ratio (again common ion effects may play a significant role at a liquid to solid ratio of 7:1).

Rigorous laboratory evaluation of these shake tests may result in the modification and refinement of suggested test procedures. Thus, while it is still possible, indeed probable, that no single test procedure will perfectly fulfill all of the requirements under section 3001 of the Resource Conservation and Recovery Act, these tests do represent a starting point for the solution of a complex problem.

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APPENDIX I

IU CONVERSION SYSTEMS, INC.
MODIFIED 48-HOUR SHAKE TEST

1. SCOPE

1.1 This method covers the determination of both the surface washing and the long-term diffusion-controlled leachate properties of a soil or waste material. The procedure is to establish representative values of the surface washing and the long-term diffusion-controlled leachate properties of a soil or waste material as placed in embankments, landfills, and other disposal or use sites. Such values can be used in the evaluation of the environmental impact of disposal or use sites. As tested these properties result from prolonged water contact both on the surface of the soil or waste materials and on a portion of the interior of a mass of soil or waste material as limited by the permeability of the material. In an actual site prolonged water contact may not be the primary leaching mechanism. The data derived from this procedure should be carefully interpreted with this fact in mind.

2. FUNDAMENTAL TEST CONDITIONS

2.1 The following test conditions are prerequisites:

2.1.1. Continuity of water movement during test with constant rate of water movement,

2.1.2 Water used in test shall be representative of water specific for the field site or Type II grade reagent water as defined by ASTM standard D1193,

2.1.3 Relative density and permeability of soil or waste material evaluated in test shall approximate relative density and permeability of soil or waste material as placed or as anticipated in the field site.

2.1.4 Dry weight of test specimen plus volume of water used in test shall be known accurately.

3. APPARATUS

3.1 Variable Speed Reciprocating Shaker equipped with box carrier large enough to hold the leaching containers used. The shaker shall be suitable for long-term continuous duty use and capable of being set to a shaking rate of 60 to 70 one-inch strokes per minute.

3.2 Membrane Filter Assembly - A borosilicate glass or stainless steel funnel with a flat, fritted base of the same material, and membrane filters (0.45μm pore size) to fit. The filters shall be prepared in accordance with ASTM D1888, section 17.3.1.

3.3 Suction Flask, at least 500 ml capacity.

3.4 Polyethylene Containers, at least 3000 ml capacity, capable of being sealed watertight.

3.5 Balance capable of weighing at least 1000 g, with a sensitivity of 0.1 g.

3.6 Graduated Cylinders, 1000 ml capacity and 20 ml. capacity.

3.7 Drying Oven, adjustable to a temperature of 104°C (219.2°F)±1°C (1.8°F).

3.8 Vacuum Pump, minimum capacity of 1.67×10^{-5} min/atmospheric cm^3, attainable vacuum of 0.1 microns Hg.

SAMPLE

4.1 From the material to be tested which is at the moisture content present or anticipated in the field, select a representative sample for testing equal to an amount approximately twice that required for the shake test. When simulating an actual field placement of stabilized soil or waste material, the relative density and permeability coefficient of the material should be known so that these values can be compared to the actual field values. ASTM D2049 and D2434 give methods for determining relative density of cohesionless soils and permeability coefficient of granular soils.

5. PREPARATION OF SPECIMENS

5.1 Take a small portion of the sample selected as prescribed in 4.1 for water content determinations according to ASTM standard D2216. In the case of waste materials containing components with water of hydration, the drying temperature should be modified to 37.8°C (100°F)±1°C (1.8°F) to avoid removing any water of hydration during moisture content determinations.

5.2 Take portions of the sample selected as prescribed in 4.1 such that five specimens weigh 125g ± 13g dry weight and one specimen weighs 500g ± 50g dry weight. In the case of monolithic stabilized soils or waste materials, the samples should be circular slices from a standard Proctor or 3" x 6" cylinder. Weigh specimens. Record wet weight of each specimen. Calculate and record dry weight of each specimen.

6. PROCEDURE

6.1 Place each of the specimens of known weight in polyethylene containers.

6.2 Measure six aliquots of water as defined in 2.1.2 such that the ratio of ml of water to g, dry weight of test specimen is 4 to 1 for each of the specimens. Dry sample weights other than those indicated in 5.2 may be used where necessary, so long as the ratio ml of water to g, dry weight, of test specimen is maintained at 4 to 1. Record measured water volume in liters for each test specimen.

6.3 Add the measured water to each of the specimens in the polyethylene containers.

6.4 Seal containers and place in box carrier of the reciprocating shaker at an oscillation rate of 60 to 70 one-inch strokes per minute. Be certain that placement of sample in container and container on shaker allows for maximum water movement.

6.5 Prepare six leachates in accordance with the following.

6.5.1 Shake one container with 125g sample for 1 hour. Note and record the condition of test specimen, being sure to include comments on physical deterioration. Immediately vacuum filter all leachate using membrane

filter assembly prepared as in 3.2. Filters should be prepared plain white filter discs of the prescribed pore size. Where sample bottles are employed for sample collection, the entire contents of a sample bottle should be filtered.

6.5.2 Shake one container with 125g sample for 2 hours. Filter as in 6.5.1.

6.5.3 Shake one container with 125g sample for 4 hours. Filter as in 6.5.1.

6.5.4 Shake one container with 125g sample for 8 hours. Filter as in 6.5.1.

6.5.5 Shake one container with 125g sample for 24 hours. Filter as in 6.5.1.

6.5.6 Shake container with 500g sample for 48 hours. Let test specimen settle for 5 minutes after stopping shake apparatus. Note and record the condition of test specimen, being sure to include comments on physical deterioration. Sample a portion of leachate using a pipet of suitable size. Reserve this portion for determination of particulate and dissolved matter in accordance with ASTM D1888. Filter remaining leachate in accordance with 6.5.1.

6.6 Chemically analyze the six leachate samples according to the schedule outlined in Table I. This schedule represents a recommended minimum analysis program. Depending on test requirements and applicable regulations, component analyses may be omitted and added as required. These analyses should be performed according to the appropriate ASTM standard methods. Record all analysis results, expressing pH in standard pH units and all other parameters in mg/l of the specified constituent. Phenolphthalein alkalinity and total alkalinity shall be expressed as meq/l and hardness shall be expressed as epm, in accordance with the ASTM standards indicated in Table I.

7. CALCULATIONS

7.1 For each of the leachate samples, calculate and record the dimensionless weight of dissolved material leached from the test specimen according to:

$$G = \frac{(TDS)V}{2W}$$

Where G = dimensionless weight of dissolved material leached

V = volume of water added to test specimen for each shake

W = dry weight of test specimen(g)

TDS = concentration of dissolved matter in leachate (mg/l)

Using this equation, the dimensionless weight is calculated on the basis of a test specimen of 500g dry weight.

8. REPORT

8.1 The report of modified 48-hour shake test shall include the following information:

8.1.1 Project dates, sample number, location, and other pertinent information.

8.1.2 Relative density and permeability coefficient of test specimens.

8.1.3 Complete test data including the following:

8.1.3.1 Dry and wet weight of test specimens,

8.1.3.2 Volume and water added for each shake period,

8.1.3.3 Chemical analysis and dimensionless weight of dissolved material leached for each of the six leachate samples,

8.1.3.4 Comments on changes in physical condition on samples after each of the six shake periods.

TABLE A-1

IUCS Modified 48-Hour Shake Test
Chemical Analysis Schedule

Constituent	1 Hour Leachate	2 Hour Leachate	4 Hour Leachate	8 Hour Leachate	24 Hour Leachate	48 Hour Leachate
pH (ASTM D1293)	X	X	X	X	X	X
Phenolphthalein Alkalinity (ASTM D1067)						X
Total Alkalinity (ASTM D1067)						X
Hardness (ASTM D1126)						X
Sulfite (ASTM D1339)						X
Sulfate (ASTM D516)						X
Chloride (ASTM D512)						X
Dissolved Matter (ASTM D1888)	X	X	X	X	X	X
Particulate Matter (ASTM D1888)						X
Arsenic (ASTM D2972)						X
Cadmium (ASTM D2576)						X
Chromium (ASTM D1687)						X
Copper (ASTM D1688, D2576)						X
Iron (ASTM D1068, D2576)						X
Mercury (ASTM D3223)						X
Manganese (ASTM D858, D2576)						X
Sodium (ASTM D1428)						X
Lead (ASTM D2576)						X
Zinc (ASTM D1691, D2576)						X

Minnesota Pollution Control Agency
Land Disposal Leach Test - Chemical Analysis

A test procedure to be used for most types of industrial wastes to evaluate the acceptability for land disposal either in a sanitary landfill or in a separate area at a sanitary landfill.

Prior to performing a leach test, a qualitative and quantitative analysis of the waste is to be performed. The analysis should include tests for total solids content, pH, chemical oxygen demand, and metals. Results for the metals analysis shall be determined with an accuracy of 0.1 mg/l. Different parameters may be required depending on the specific waste tested.

To assess possible impacts upon ground water quality, the following test should be performed to determine the approximately characteristics of leachate generated from a landfill containing an industrial waste. Two diluents are used to approximate conditions both in a sanitary landfill or in an area segregated from refuse deposits.

1. Vigorously shake 25 grams of waste with 1 liter of diluent in a 2000 ml glass separatory funnel for 60 seconds (one diluent consisting of buffered acetic acid solution and the other diluent consisting of deionized distilled water).

2. Cover and let the mixture stand for 24 hours.

3. At the end of 24 hours, shake the mixture vigorously for 60 seconds.

4. Filter the mixture through medium porosity ashless (less than .01% ash) filter paper. The filtered mixture will then be called leachate. Discard first 10 mls of leachate.

5. The leachate is then analyzed for constituents found in the qualitative and quantitative analysis. The porosity of filter paper used, methods of analysis, and final pH and solids content should be reported.

*Solution should be formulated as follows:

1. Measure 49.21 gms. HOAc into a 2 liter container.

2. Add 37.21 gms. NaOAc

3. Add enough deionized distilled water to make a total solution of 1 liter - stir.

4. Solution will have a pH of 4.5.

* Not necessary unless waste is to be mixed with domestic wastes.

UNIVERSITY OF WISCONSIN SHAKE TEST

Samples are first separated into a liquid and solid phase by pressure filtration under an inert gas (e.g., N_2) using a 142 mm 0.45μ glass filter. Some samples, particularly ones containing fibrous materials (e.g., paper, cloth) may require filtration through a wire or plastic screen prior to pressure filtration. Solids collected in this step are combined with those of the second. The filtrate resulting from this first separation is analyzed for the parameters of interest (e.g., pH, pε, heavy metals).

A representative 28.6 gram sample from the above separation scheme (ground only to the extent necessary to place the sample in the container) is mixed with 200 ml of eluant (1:7 ratio by weight - see below) in a closed container and mixed (rotating shaker (Knabe, 1976)) for 24 hours. The mixture is then filtered through a 0.45μ filter. 200 ml of fresh eluant is added to filtered solid and the process repeated. The solid is leached a total of three times with fresh eluant over a three day period. The resulting filtrates are analyzed separately for the parameters of interest (e.g., pH, pε, heavy metals).

No effort is made to control the temperature under which the solid is extracted (other than ambient laboratory conditions).

Eluant Composition

0.15M	Acetic Acid
0.15M	Sodium Acetate
0.05M	Glycine
0.024M	Iron (II) Sulfate
0.008M	Pyrogallol